# Tappi

PUBLISHED BY THE TECHNICAL ASSOCIATION OF THE PULP AND PAPER INDUSTRY

OCTOBER 1951

# *Interesting Facts about Paper*

In the decade 1825-1835, paper was made from hay in France, from peat in Ireland, and from the aloe plant in Mexico—where a law was passed to prohibit the use of any other material for paper.

## interesting facts about DIRECT CHINOLINE

DIRECT CHINOLINE is the brightest and greenest direct yellow. Possessing excellent solubility, level dyeing and good light fastness, it is recommended for use in coloring bond, book and cover papers to produce bright canary; or to produce bright greens in combination with Quinizol Blue BP Dustless.

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AMERICAN Cyanamid COMPANY

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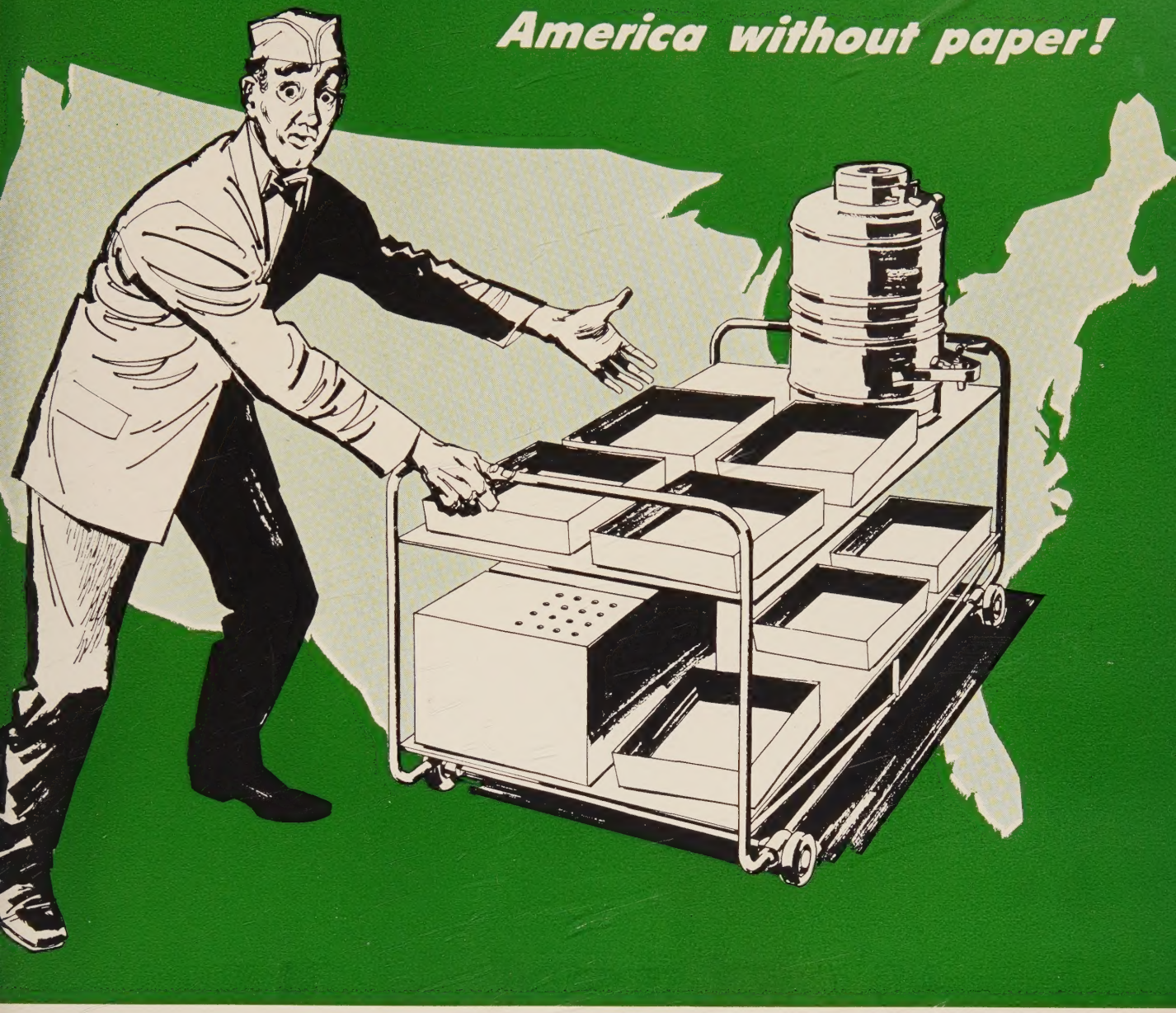
# IMAGINE...

## America without paper!



*No more paper!* No paper cups, plates, containers, or protective wraps. No paper napkins . . . not a single waxed paper bag. What happens, then, on the *food front?* Mobile food units would fail to serve industry . . . canteens would close overnight. And a lack of packaging materials . . . labels, liner boards, parchments, wrappers for frozen foods . . . would affect virtually everyone. Foods today are processed at the peak of their perfection . . . served with utmost convenience, under sanitary conditions. But it takes paper to help make this possible. Daily, in countless ways, America *depends* on paper! Use it wisely . . . protect its production . . . keep American strong.

## America depends on PAPER

BELOIT IRON WORKS · PAPER MACHINERY · BELOIT, WIS., U.S.A. ·

PREPARED IN THE PUBLIC INTEREST BY BELOIT IRON WORKS, BELOIT, WIS.
MAKERS OF HIGH-SPEED, HIGH-PRODUCTION PAPER MACHINERY SINCE 1858

**CAN YOU USE REPRINTS?** This is one of a series of messages Beloit is running in *Fortune* Magazine to remind the U.S. of paper's importance. Reprints for bulletin boards and mailing available. Write to Beloit Iron Works, Beloit, Wis.

# COLORED wrappings are advertisements for the store

Smart retailers have discovered that *colored* wrappings give them an *extra way to advertise.* Distinctively colored cartons, wrapping paper and shopping bags identify the store at a glance. Each one is an advertisement on the streets, in buses and streetcars . . . and in the home.

But many retailers are still using nondescript paper and boxes. Tell them about the advertising plus *your wrappings—in color*—can give them . . . and corner your share of a big potential market.

Our Technical Staff will be glad to help you choose the proper dyes, from a large selection of excellent, light-fast, economical dyestuffs. Write today for complete information to E. I. du Pont de Nemours & Co. (Inc.), Dyestuffs Division, Wilmington 98, Delaware.

***More color makes more business ...for your customers and you***

**DU PONT BASIC DYES**

Du Pont Safranine T Ex. Conc. 125%
Du Pont Rhodamine 5GDN Extra
Du Pont Fuchsine N
Du Pont Rhodamine B Extra
Du Pont Auramine Conc.
Du Pont Chrysoidine GN
Du Pont Victoria Pure Blue BO
Du Pont Methylene Blue ZX

**DU PONT ACID DYES**

Du Pont Orange 11 Conc.
Du Pont Orange RO

**DU PONT DIRECT DYES**

Du Pont Purpurine 4B Conc.
Pontamine* Fast Scarlet 4BS Conc. 150%
Pontamine* Yellow SXP Conc.
Du Pont Stilbene Yellow G Conc.
Du Pont Stilbene Yellow GCB Conc.
Pontamine* Fast Orange WS Conc. 175%
Pontamine* Orange R Conc.
Pontamine* Black E. Double
Pontamine* Brown D3GN Conc. 125%

*REG. U. S. PAT. OFF.

Du Pont Dyestuffs

DU PONT

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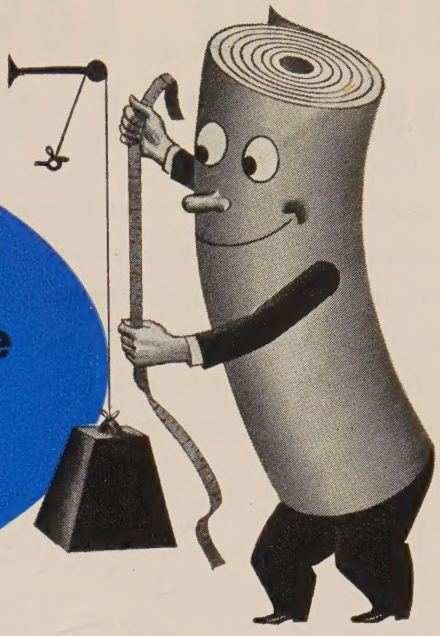
BETTER THINGS FOR BETTER LIVING . . . THROUGH CHEMISTRY

# SCIENTIFIC CONSTRUCTION
## Makes the Big Difference in DRYER FELTS



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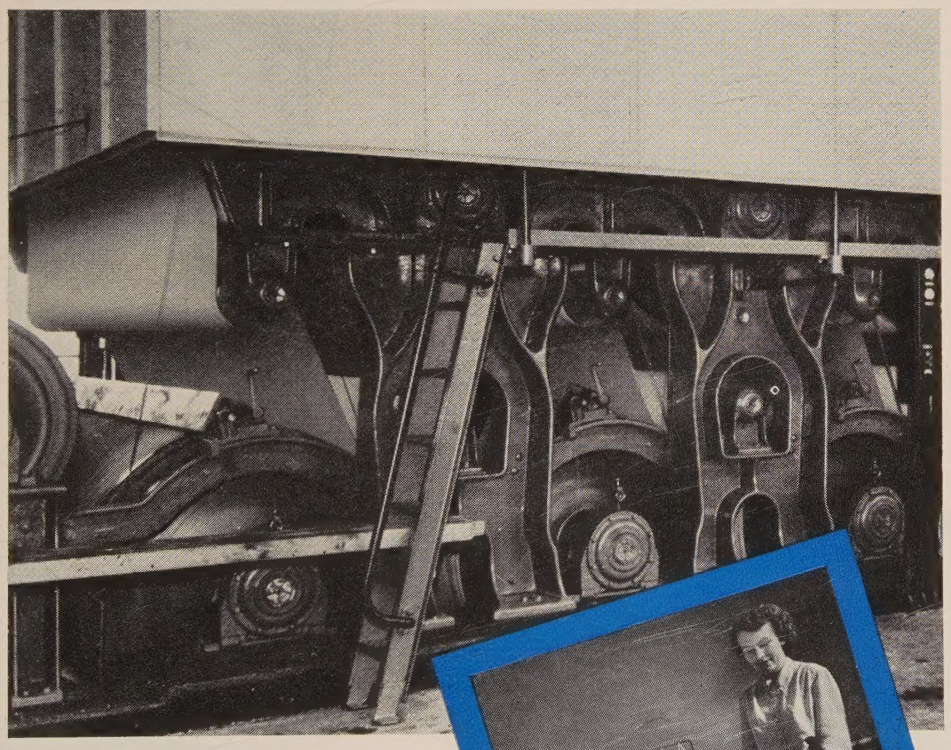
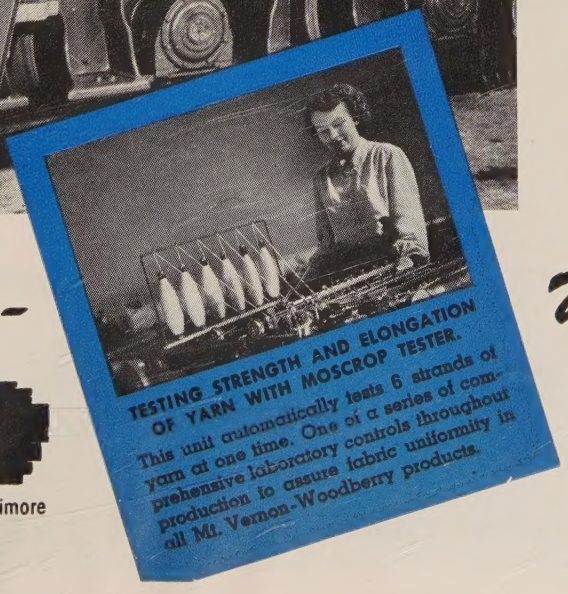
REINFORCED
DRYER FELT

**Gives You Scientific Construction**





TESTING STRENGTH AND ELONGATION OF YARN WITH MOSCROP TESTER.
This unit automatically tests 6 strands of yarn at one time. One of a series of comprehensive laboratory controls throughout production to assure fabric uniformity in all Mt. Vernon-Woodberry products.

Asbestos yarns woven at scientifically determined intervals into the face of Woodberry 887 heavy duty dryer felts means longer wear, lower steam consumption, increased porosity, finer paper quality.

**AT YOUR SERVICE**

Mt. Vernon-Woodberry's staff of textile engineers is available on request to help you with your problems in development or application of industrial fabrics.

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# POSITIVE, LOW COST CONTROL OF INDUSTRIAL WASTES...

**Effective, positive treatment for phenol, cyanide and other noxious industrial wastes—without excessive installation and operating costs—is now available through the Mathieson Chlorine Dioxide Process. Existing installations, handling both large and small waste volumes, attest to the efficiency and economy of this treating method.**

## Mathieson's Chlorine Dioxide Process

### * Low Capital Investment

A Chlorine Dioxide system to handle an average waste output can be installed for $2000-$3000, and amortization charges are negligible. The equipment consists only of a small holding tank, a chlorine dioxide solution generator and the metering equipment for the chlorine and sodium chlorite solutions.

### * Simple Installation

The Chlorine Dioxide system, being extremely compact, can be quickly and easily fitted into the disposal facilities. No special housing is necessary to contain the equipment.

### * Minimum Maintenance

The simplicity of the Mathieson Chlorine Dioxide equipment minimizes maintenance and no special technical supervision is required for operation. The chlorine dioxide is fed automatically at the pre-determined rate for safe, positive control.

**Mathieson's background of experience, accumulated over many years in the field of sanitation is available to you. Write for information about the Chlorine Dioxide Process. Mathieson Chemical Corporation, Baltimore 3, Maryland.**

Mathieson CHEMICALS

9456

SERVING INDUSTRY, AGRICULTURE AND PUBLIC HEALTH

OCTOBER 1951

# Tappi

VOL. 34 · NO. 10

*Published monthly by the Technical Association of the Pulp and Paper Industry*

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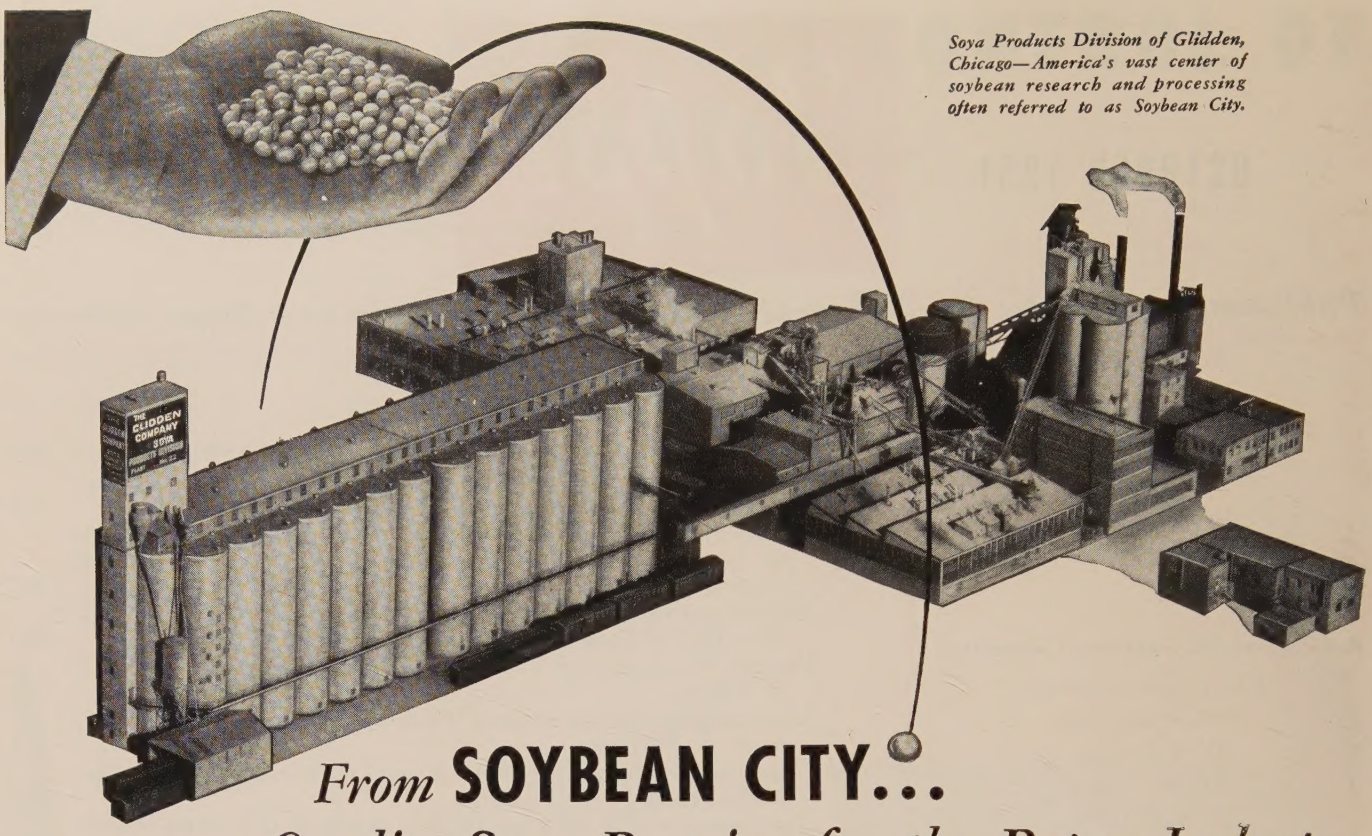
Published monthly by the Technical Association of the Pulp and Paper Industry at 20th and Northampton Streets, Easton, Pa. Editorial and advertising offices, 122 East 42nd Street, New York 17, N. Y. Articles for publication and communications regarding the editorial content of *Tappi* should be addressed to the Editor at the editorial office. Statements and opinions expressed in articles and editorials appearing in *Tappi* are those of the contributors, and the Technical Association of the Pulp and Paper Industry assumes no responsibility for them. Subscription: U. S. and possessions, $7.50; Canada, $8.25; Pan American Union, $9.00; Other Foreign, $10.00. Single copies to members of TAPPI, $0.75; Nonmembers, $1.00. Entered as second class matter January 27, 1949, at the Post Office at Easton, Pa., under the act of August 24, 1912. Copyright, 1951, by the Technical Association of the Pulp and Paper Industry. An index of the technical articles appearing in the magazine appears in the Industrial Arts Index and the Engineering Index.




*Soya Products Division of Glidden, Chicago—America's vast center of soybean research and processing often referred to as Soybean City.*

# *From* SOYBEAN CITY...

## *Quality Soya Proteins for the Paper Industry*

**Glidden ALPHA* PROTEIN**

**Glidden PROSEIN***

Coating papers with this chemically isolated, soya protein adhesive definitely *adds* to their quality. Paper coaters everywhere have learned from experience that it introduces efficiencies which actually lower coating costs! Here are just a few of the unusual properties of Glidden Alpha* Protein which it will pay *you* to know about:

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- Glidden Alpha* Protein alkaline-cut adhesive permits addition of formaldehyde to coating colors to make the finished paper water resistant.
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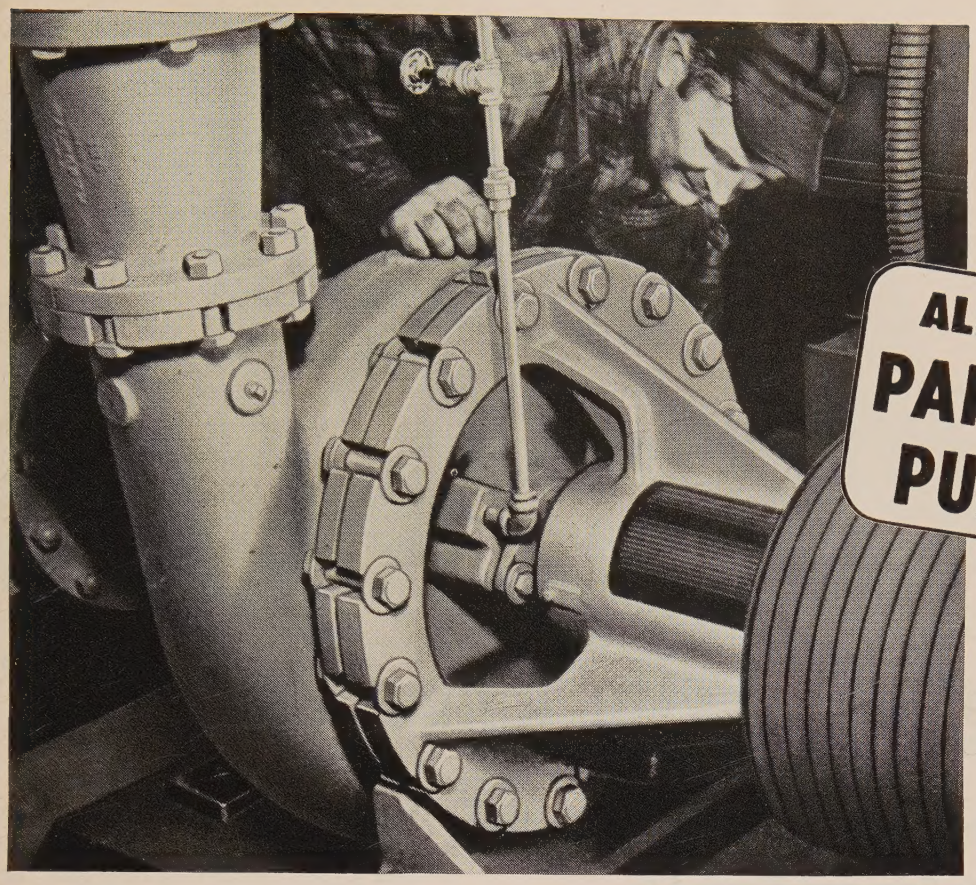


**ALLIS-CHALMERS PAPER STOCK PUMP UNIT**

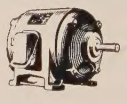
# Accessibility Like This Cuts Maintenance Costs

SEE HOW EASY IT IS to work on the packing and clear water seal of this Allis-Chalmers Type PW Paper Stock Pump. And notice that the casing bolts are in slots instead of holes. This makes it possible to remove the rotating element in five minutes and replace it in the same quick time. Neither suction nor discharge piping need be disturbed. Thus maintenance is easy and fast, maintenance costs are low.

Heavy construction designed especially to withstand the loads imposed by pumping heavy stock and special materials to suit the characteristics of the stock being pumped keep the necessity for maintenance down. Many parts are interchangeable on several sizes of pumps so spare parts inventory is low regardless of the number of pumps you operate.

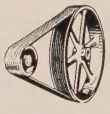
## FREE ENGINEERING HELP

Allis-Chalmers pump representatives are thoroughly familiar with all types of paper making processes. One of these competent application engineers will be glad to help you with your pumping problems — or with your problems involving any other of the many paper making processes for which Allis-Chalmers manufactures equipment. Call your nearby Allis-Chalmers District Office, or write Allis-Chalmers, Milwaukee 1, Wisconsin. Ask for bulletins 08B7112 and 08B6725. A-3406



MOTORS

*STREAMBARKER*



*TEXROPE* V-BELT DRIVES

VIBRATING SCREENS

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ROTARY KILNS

*AND OTHER EQUIPMENT FOR PAPER MAKING . . .*

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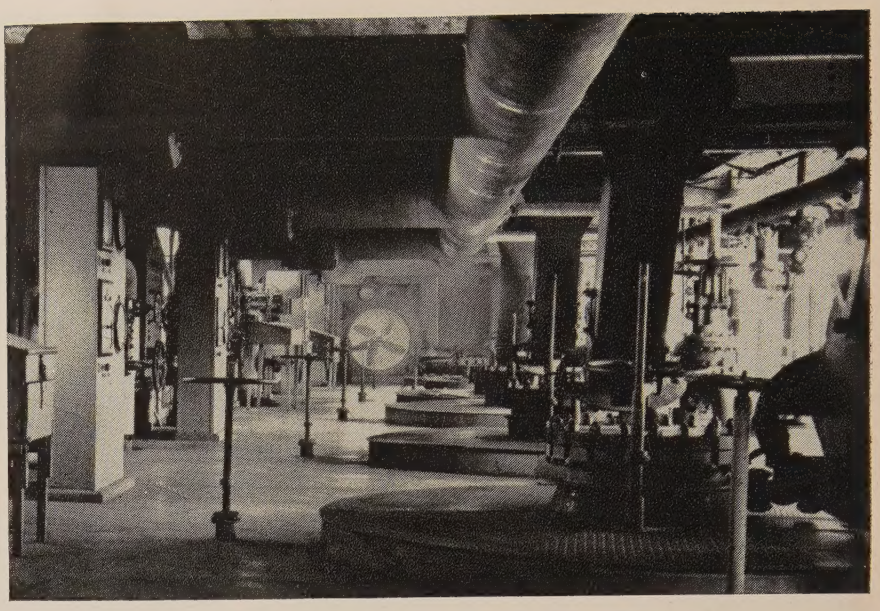


**THE CORRECT COMBINATION FOR SUCCESS**—In addition to good instrument performance the success of this installation is also due to the willing and complete cooperation of the Brunswick Pulp and Paper Company with the Bristol organization in the engineering, installation, and operation of the control equipment.

# "Outstandingly Successful Automatic Control"

## Bristol Digester Control Gives Complete Satisfaction at Brunswick Pulp and Paper Co.

As reported by Brunswick, the results obtained from automatic control system include (1) saving in steam, (2) pull-over of liquor minimized, (3) ideal cooking schedule accurately and consistently repeated, (4) practically no maintenance required, (5) results fully satisfactory.

Like all Bristol control systems, this one is simple, adaptable. Operating men get familiar with it fast. Control panel units can be installed side-by-side to form a continuous panel for controlling an entire digester house, and can be enlarged to cover more digester.

### Bristol Instruments Get the OK in Mills from Coast to Coast

Experience at Brunswick Pulp and Paper Company is typical of the performance of Bristol Recording Instruments and Automatic Control Systems in Paper Mills from coast to coast.

Bristol manufactures a complete line of automatic controlling, recording, indicating and telemetering instruments and component equipment for the Pulp and Paper Industry to take care of applications requiring from only one or a few instruments to those requiring extensive instrument control panels.

**NEW SERIES 500 INSTRUMENTS ARE NOW AVAILABLE.** Products of over 60 years of instrument experience, they are extremely simple in construction and will withstand the severest service. They require practically no maintenance — anybody can take care of a Bristol Series 500 instrument.

### Bristol Has the Resources Needed to Give You the Best in Instrument Engineering

Bristol has developed techniques and facilities for handling even the most difficult and unusual control problems. Our engineers will relieve you of many worries by providing layout drawings and piping and wiring diagrams. We furnish panels in finished form with all internal piping and wiring complete. All you have to do is make main power and air-line connections. Our engineers stay with the job until operating satisfactorily.

Make use of Bristol resources. Write for Bulletins. THE BRISTOL COMPANY, 102 Bristol Road, Waterbury 20, Conn.

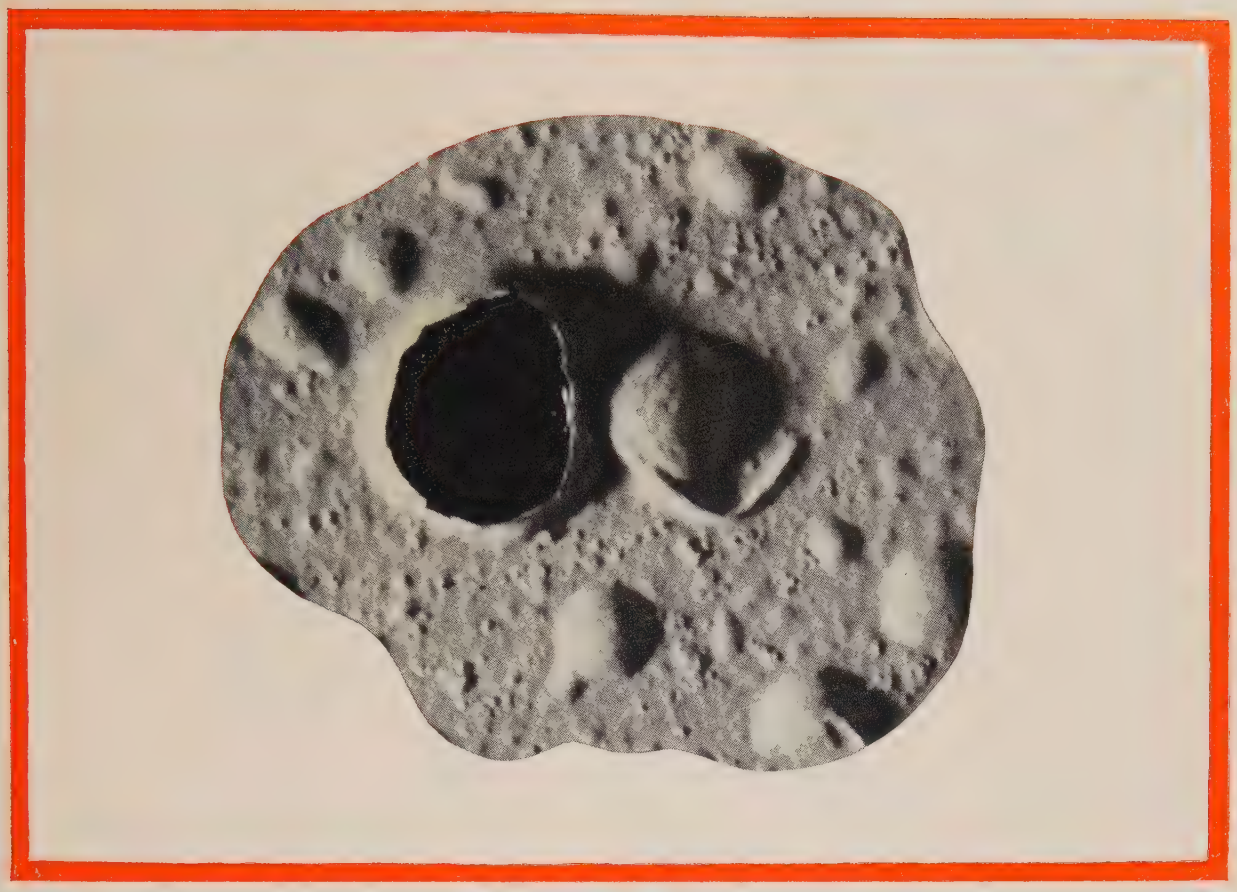
### Quick Facts About Bristol Alkaline Digester Control System

Bristol Alkaline Digester Control System is used to automatically control digestion of Southern pine and Northwestern fir and hemlock in direct and indirect-steamed digesters, with either forced or natural circulation of both long and short cooks. *Installation requires no changes in digester equipment. It adapts itself to the digester, resulting in lower installation cost.* It is also adaptable to changes in operating conditions.

THE DEPENDABLE GUIDEPOST OF INDUSTRY

**BRISTOL**

AUTOMATIC CONTROLLING. RECORDING AND TELEMETERING INSTRUMENTS



# A Penny Saved is a Penny Earned?

Not always! Here's a quick picture of the "saving" of a few pennies on a protective coating! Here's a close-up of the costly corrosion that results!

When it comes to protecting your equipment against chemical attack — don't be "penny wise and pound foolish". Use a truly chemical-resistant coating. Use TYGON "Series TP" PAINT.

In pulp and paper mills, TYGON PAINT does an excellent job of protecting such equipment as grinders, refiners, digesters, "black liquor" storage tanks, washing, mixing and bleaching tanks, "stuff" chests, mixing and "head" boxes, presses, pumps and piping, against corrosive fumes and spillage. Structural steel, walls, and ceilings also benefit from TYGON protection.

Caustic soda, soda ash, sulfur dioxide, calcium bisulphite, lime, ammonia, sulfuric acid, bleaching powder, chlorine, alum, barytes, rosin, casein, organic dyes and inorganic pigments are a few of the paper making chemicals resisted by TYGON.

Available in a wide range of colors, TYGON PAINT is easily applied and quick drying — requires no more than normally good surface preparation. Once dry, its film is tough, smooth, flexible and non-flammable. It's easy to clean and seemingly ageless, too.

Properly applied, TYGON PAINT is low cost insurance against costly corrosion.

Write, today, for full details and technical data. Ask for Bulletin 720.

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*100 YEARS is a* large *sector of time. Back in 1851 when Charles Morningstar, grandfather of Joseph Morningstar, present head of Morningstar, Nicol, Inc., founded the company, the California Gold Rush was at its height; Millard Fillmore was President of the United States, Daniel Webster was Secretary of State. Henry Clay's effort toward the admission of New Mexico and Utah as Territories had just succeeded. From a humble beginning, so long ago, the Morningstar Company has grown until it now has operations in 20 states. Especially rapid progress and expansion has occurred during the past decade. In addition to the domestic sales and manufacturing activities, Morningstar, Nicol, Inc. also imports Tapioca Flour from Brazil, Arrowroot from the West Indies, as well as Starches and Tropical Gums. You will find us keenly alert to every opportunity to render a valuable service to the Paper Field.*

# IF IT'S A DEXTRINE, STARCH OR ADHESIVE PROBLEM

## "Put it up to MNI"

## Let Our Paper Department Experts Give You Valuable Aid On . .

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2. TAPIOCA FLOURS
3. CONVERTED POTATO STARCHES
4. LAMINATING ADHESIVES
5. BAG PASTES
6. CORRUGATING STARCHES
7. MANNOGAL (Mannan-Galactan) PRODUCTS

Morningstar's modern laboratory and manufacturing facilities are now ready to give far more effective aid to the Paper Industry! Our enlarged Paper Department is now under the supervision of Mr. Jerome P. (Jerry) Strasser who is directing the development and application of our Starch Specialties and Adhesives for the paper trade. Mr. Strasser, together with MNI Laboratory and Technical Field Men can lend you highly effective and valuable aid on your Dextrine, Starch and Adhesive problems. Without obligation, write TODAY! Ask for suggestions, ideas, samples and cost estimates on your needs. Get all the advantages which only MNI's extensive experience and facilities can give.

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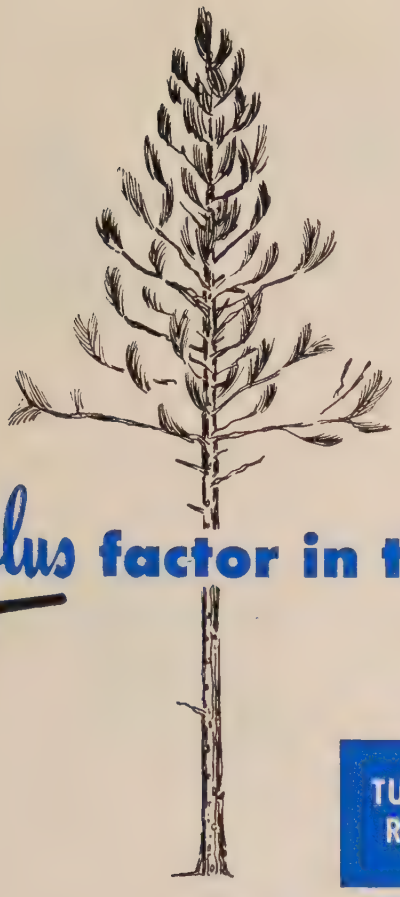
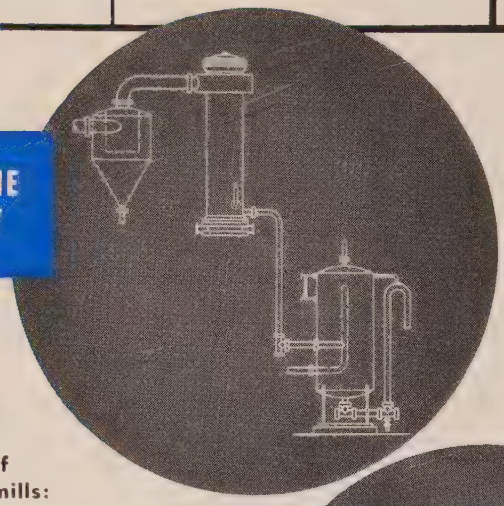
CHICAGO 16, ILLINOIS



a *plus* factor in the paper dollar



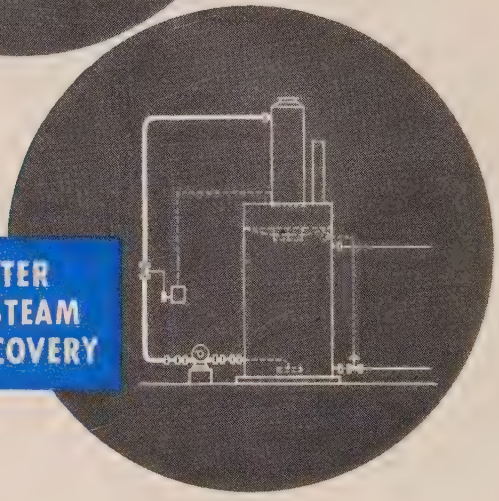
TURPENTINE RECOVERY

Recent installations by these three leading paper manufacturers confirm once again not only the sound economics of turpentine and digester heat recovery but also the continued acceptance of Foster Wheeler equipment by pulp mills:

RIEGEL PAPER CORPORATION
Acme, North Carolina

ST. REGIS PAPER COMPANY
Eastport, Florida

WEST VIRGINIA PULP & PAPER COMPANY
Covington, Virginia



DIGESTER BLOW STEAM HEAT RECOVERY

These properly engineered systems enhance the credit side of the ledger in two ways.

First, two to four gallons of crude turpentine, a particularly valuable by-product on today's market, are recovered from every ton of pulp.

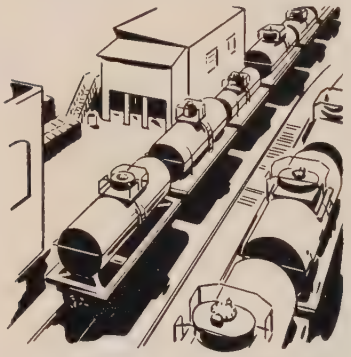
Second, valuable Btu's from digester blow steam are recovered to heat mill water for pulp washing.

Bulletins describing these Foster Wheeler recovery systems will gladly be sent on request.

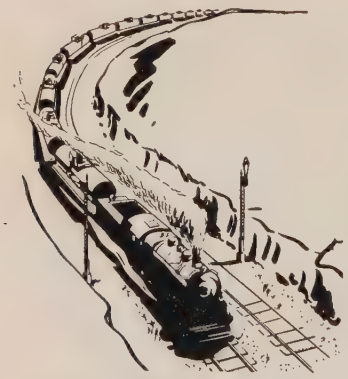
FOSTER WHEELER CORPORATION • 165 BROADWAY, NEW YORK 6, N. Y.

FOSTER WHEELER

**PURITY . . .** From the efficient Hooker "S" Cells we produce chlorine and caustic soda of a uniformity that enables you to keep bleach preparation methods constant, for consistent bleaching results.



**PACKAGING . . .** Hooker Chlorine and Caustic Soda are shipped in specially conditioned tank cars, carefully inspected before shipment to guard against leakage and give you trouble-free, safe unloading.



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# THE PRESIDENT'S PAGE

Of all the changes that have taken place in TAPPI during the past ten years, probably none reflects its growth more clearly than the development of the regional meetings.

Formerly, the "Fall Convention" was a smaller edition of the one that is held every year in February; but today it has been replaced by a whole series of meetings, each one of them of greater significance than the single meeting that used to be held in the Fall.

We all realize that the Annual Convention held in February is just as essential as ever. It represents one of the most important means of tying together the work of the National Association, in spite of some of the disadvantages that are unavoidable in the crowded schedule that must be maintained.

Moreover, it is only at the February Meeting that all of the committees are represented and have a chance to meet at the same time; it is only then that the representatives of the Local Sections can meet to discuss their common problems.

However, we must not permit its importance to make us lose sight of the advantages that are presented by the regional meetings. These are drawn up along functional lines and offer committee chairmen exceptional opportunities to strengthen the work of their committees.

As each functional meeting has increased in size, there has been a tendency for it to divide into other meetings of more limited scope but with a greater chance for a more exhaustive coverage of the subjects to be considered.

Thus, we have already held, not only in the Fall, but at other times during the year, conferences devoted to fundamental research, engineering, alkaline pulping, acid pulping, mechanical pulping, coating, plastics, fibrous agricultural residues, testing, containers, and packaging. Plans are being made for similar meetings along other lines.

At these meetings there is ample time for a thorough consideration of the problems being discussed; in fact, there has been a strong tendency recently to plan an entire meeting around one particular phase of the subject and to treat it exhaustively.

Here is an opportunity for each chairman to call a meeting in connection with the conference most closely allied to the interest of his committee. The chances are strong that most of the members of this committee would be attending the conferences anyway, and the others would find it worth their while to attend the committee meeting with the added advantage of attending a conference so close to their interest.

There are other advantages in planning committee meetings in this way. Men are able to attend these regional conferences that are unable to be in New York because mills are limited in the number of men that they can send in February without stripping their technical department of too many key men.

Thus, these regional conferences provide opportunities for attendance by the younger men who are anxious to serve on committees. Moreover, there is ample time for the chairmen to arrange for more than one meeting of his committee if it appears desirable.

As the work of one of these committees grows, it may reach a point where it may appear advisable for the committee to consider sponsoring its own regional meeting.

Just a word to each member of TAPPI who has never attended one of these functional conferences. He should do so to experience the satisfaction of attending a meeting devoted entirely to a subject in which he is particularly interested. Here is an opportunity to gain knowledge that cannot be obtained in any other way and that may prove of inestimable value to him and to his company.

K. P. Geohegan
*President of TAPPI*

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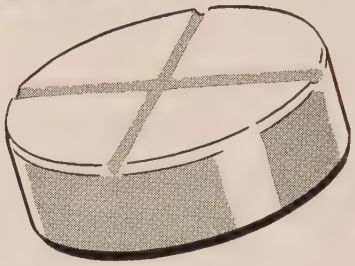

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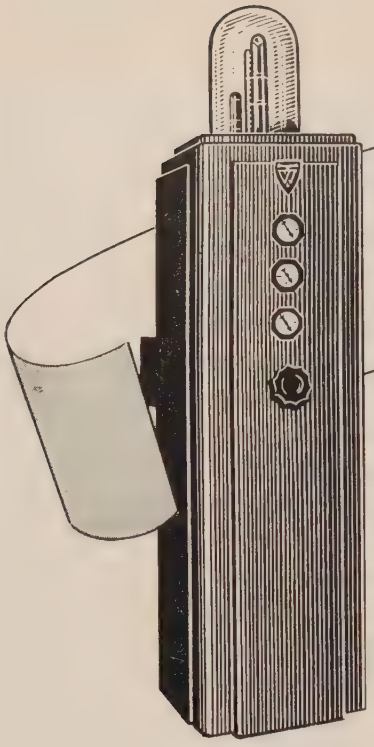

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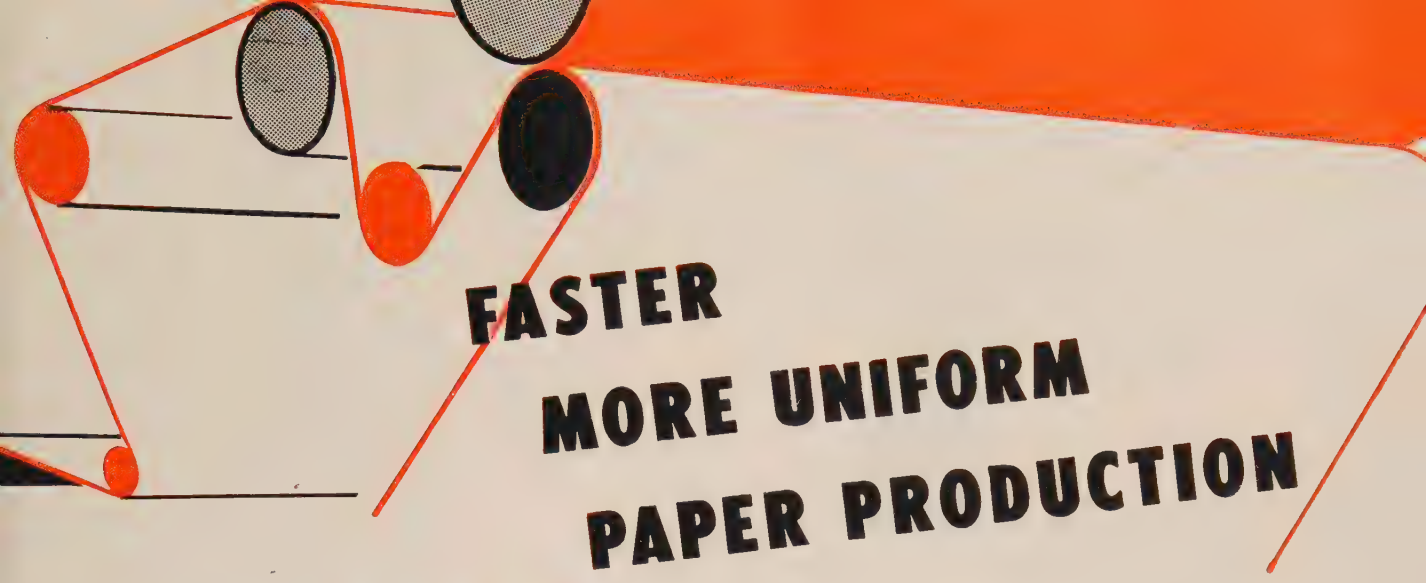

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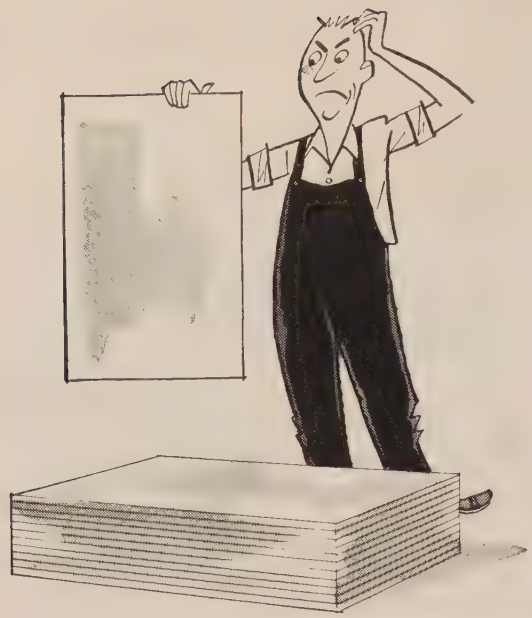

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# Food Yeast from Sulphite Liquor

GORDON C. INSKEEP, A. J. WILEY, J. M. HOLDERBY, and L. P. HUGHES

THE disposition of spent liquors from the sulphite pulp industry has been the subject of a tremendous volume of research during the past 70 years. Pulp mills, individually and collectively, and research centers, public and private, have spent millions of dollars on the spent liquor problem.

In the broadest sense two general lines of approach have been used: (1) treatment of the liquor to minimize the deoxygenating effect of its wood sugar content on receiving streams; and (2) utilization of the raw materials present in the spent liquor. Unfortunately, a completely satisfactory solution still remains to be found.

The original practice, which has been continued in most cases, was to discharge the spent liquor as produced, with no pretreatment, into the streams. Simple modifications of the principle of discharge to streams have been suggested and found applicable in a few situations.

Where very large bodies of dilution water are available some mills have been able to build special discharge lines to achieve maximum dilution. This was done at Rayonier's Fernandina, Fla., plant, which pipes liquor 5 miles into the Gulf Stream, and at Camas, Wash., where spent liquor is distributed in the central currents of the large Columbia River. Another idea which may be feasible for some smaller mills involves storage of liquor in ponds and discharge during periods of high-stream flow (*1*).

Although stream improvement has usually been and still remains the immediate objective of research efforts, increasing pressure from the laws of economics has emphasized the importance for concomitant utilization of this great amount of potential raw material.

Investigations into sulphite liquor treatment have resulted in processes utilizing the liquor itself or its components such as the lignin. Vanillin, oxalic acid, tanning material, road binders, dispersing agents in concrete, alcohol by fermentation, yeast by fermentation, and others have been made from sulphite liquor.

Some of these processes have been successful commercially. The Monsanto Chemical Co. announced this Spring that it is building a new plant on the West Coast for the production of vanillin from the lignin in the sulphite liquors. However, according to Hatch (*4*) it is theoretically possible to produce enough vanillin to satisfy the entire need of the United States from the spent liquor resulting from the production of 30 tons of sulphite wood pulp per day. Relatively few individual mills in the United States have a capacity below 100 tons per day. Obviously this is not the answer to the liquor disposal problem.

The same is true of the production of oxalic acid and a number of other by-products; these would provide an outlet for only a small portion of the spent liquor produced each year.

GORDON C. INSKEEP, Associate Editor, *Industrial and Engineering Chemistry;* A. J. WILEY, Sulphite Pulp Manufacturers' Research League, Inc., Appleton, Wis.; and J. M. HOLDERBY and L. P. HUGHES, Lake States Yeast Corp., Rhinelander, Wis.

Spent sulphite liquor has been utilized as a source of calcium lignosulphonate for use with Portland cement either as a grinding aid or as an addition to the concrete mix to secure the benefits of cement dispersion (*11*). Here again the quantity of liquor thus far used is negligible in the industry-wide picture.

Another approach to the problem has been evaporation with subsequent incineration of the concentrated liquor as fuel. However, using the liquor from calcium-base pulping, a high percentage of steam so produced would be required for concentrating the spent liquor to burning consistency, and the economics of the over-all evaporation and burning operation have yet to be proved commercially in the United States.

With magnesium as the pulping base, liquor is produced which breaks down to magnesium oxide when incinerated under reducing conditions; the oxide can then be reused in the pulp mill. This magnesia-base sulphite pulping process with the relatively new recycle aspects has recently been put into practice at the Longview, Wash., plant of the Weyerhaeuser Timber Co.

The fermentation approach has been used quite widely in Europe. Nearly all sulphite liquor in Germany is used to produce yeast or alcohol. However, European mills producing alcohol usually operate under a government subsidy not available to mills in this country. High operating charges and high plant investment discourage interest by any but the largest pulp mills in the United States. Furthermore, only the hexose sugars in the spent liquor are converted into alcohol by fermentation. These sugars account for 50% or less of the 5-day B.O.D., which means that this is a far from satisfactory stream improvement measure.

The fermentation of spent sulphite liquors to produce inactive dry yeast, although practiced by several plants in Europe, has been applied commercially in only one plant in the United States. This plant is operated by the Lake States Yeast Corp. at Rhinelander, Wis. The technical problems are well under control and if the economic considerations can be sufficiently improved this will be one of the more promising solutions to the spent sulphite liquor problem in this country.

Briefly, the sulphite pulping process in general use today can be described as follows:

Sulphur is burned and the gases are absorbed in a lime suspension to form a solution of calcium bisulphite containing an excess of free sulphur dioxide. Other bases, such as sodium and ammonium as well as magnesium mentioned earlier, can be used to form the cooking acid.

Wood chips are cooked in the bisulphite at temperatures from 130 to 150°C. for 6 to 18 hours. During the digestion period lignin combines with sulphur dioxide or the sulphite ion to form soluble calcium lignosulphonate. After the cooking process is completed the acid liquor containing the dissolved materials is separated from the insoluble cellulose and is discharged as spent sulphite liquor.

Somewhat over 1 ton of dissolved wood solids for each ton of pulp produced is commonly present in this spent liquor. The organic material present in the liquor is

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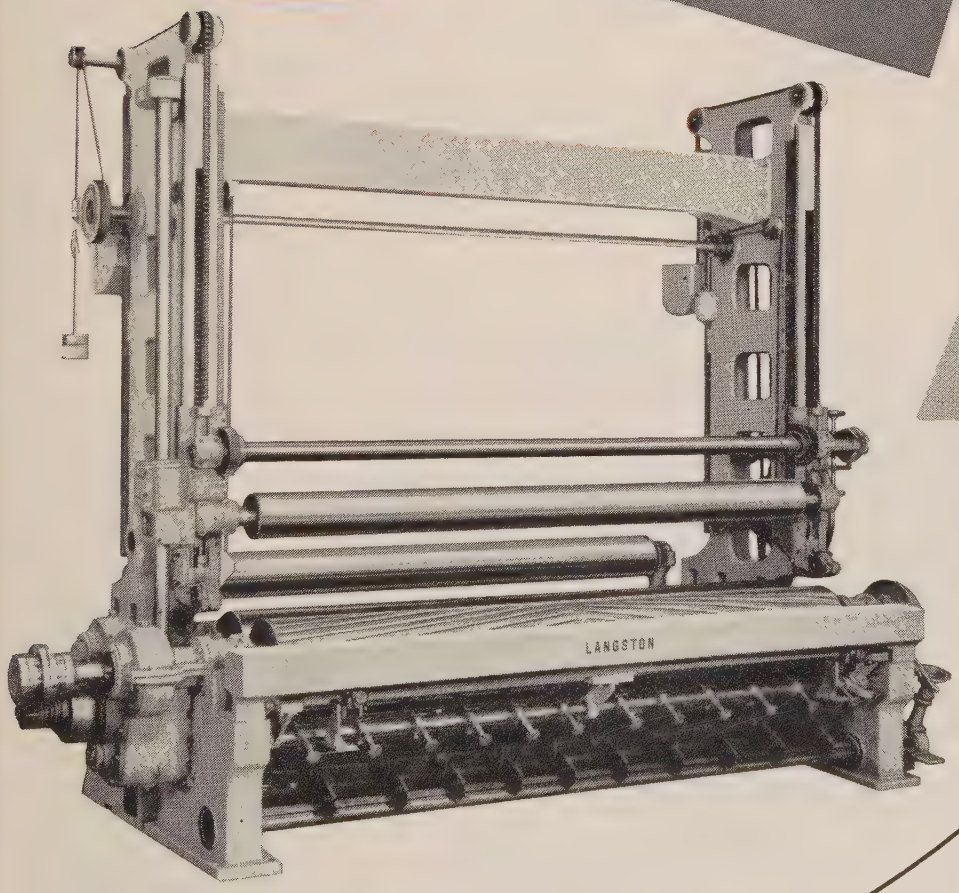

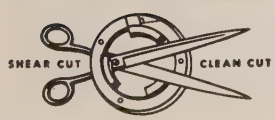


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complex; about 20% of the dissolved solids is made up of easily oxidized sugars and related products and 60% of more or less stable lignosulphonate compounds. An average composition of spent sulphite liquors from spruce wood pulping is shown in Table I.

From an average size pulp mill (100 tons of pulp per day), some 20 tons of fermentable material are produced. When this amount is fed to the microbiological flora of streams, biological oxidizing processes are stimulated into roughly equivalent demands for some 20 tons of oxygen.

The annual domestic production of sulphite pulp in the 10-year period 1940–50 is shown by Table II. The production has averaged more than 2,500,000 tons per year. From this production there are some 500,000 tons of fermentable sugar wasted each year.

**Table I. Composition of Spent Sulphite Liquors from Spruce Wood**
(Variations Based on Liquors of the Same Solids Concentration)

| | *Grams per liter* | |
|---|---|---|
| Neutralized solids | ... | 100 |
| Total sugar (as glucose) | ... | 15–22 |
| Hexose | 11–16 | ... |
| Pentoses | 4–6 | ... |
| Volatile acids (as acetic) | ... | 2–5 |
| Sulphur (all forms as $SO_2$) | ... | 8–10 |
| Total inorganic (free) $SO_2$ | 0.5–2.5 | ... |
| Organic loosely combined $SO_2$ | 3.0–5.0 | ... |
| Lignin (as lignosulphonate) | ... | 50–65 |
| Calcium | ... | 7–10 |
| Misc. compds.: solvents, aldehydes, uronic acids, resins | ... | 2–5 |

pH 1.5–3.0

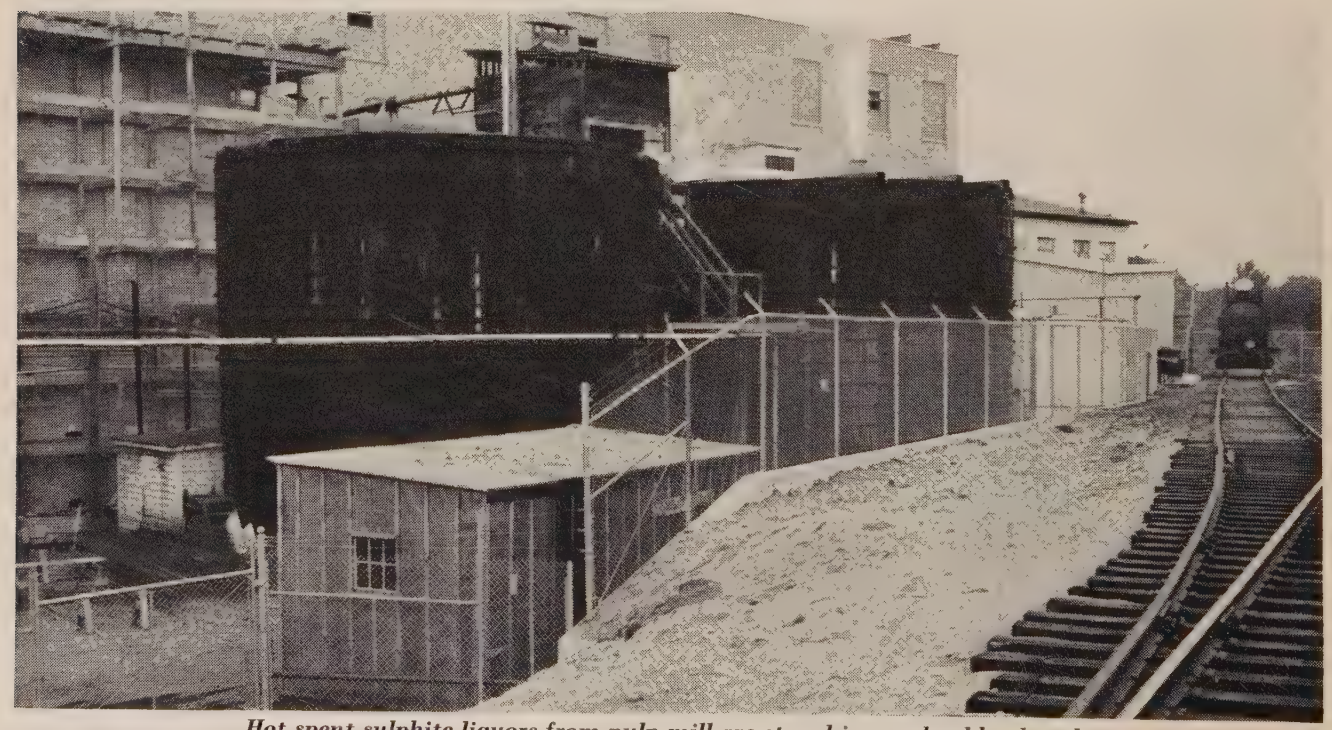
## HISTORY OF YEAST PROCESS

Early recognition of the possibilities for growing *Torulopsis utilis* as a food and feed supplement material is credited to Delbruck and his co-workers at Berlin's Institute for the Fermentation Industry during the first World War. Fink, Lechner, and Just, working prior to and during World War II at the same research center, laid the laboratory and pilot plant groundwork for growing this organism commercially. Recognition of the pentose-consuming ability made possible the utilization of the hardwood liquors from the German pulp industry to give protein products capable of relieving critical food and feed shortages of the German Reich. Under stimulus and organization of the "Four Year Plan," the process reached the commercial stage with unusual speed.

Variations of the torula yeast process were developed more or less independently by several German pulp concerns. That of Zellstofffabrik Waldhof, involving unique aeration methods, was most successful, and the German industry, near the end of World War II, was asked to develop a standardized design based on that system for all new plants. Little, if anything, concerning German commercial methods, equipment, and know-how, was available on this method of yeast production outside Germany before the technical intelligence teams entered that country in 1945. Excellent reports were then prepared by Saeman, Locke, and Dickerman (*9*), Holderby (*5*), and others; these have made the German versions of the process available generally.

A group of thirteen pulp mills in Wisconsin and Michigan, organized in 1939, and now known as the Sulphite Pulp Manufacturers' Research League, Inc., originally undertook study of the organism in this country. Microbiological processes capable of utilizing pentose sugars had not appeared feasible until then.

Active laboratory and pilot studies were initiated by this group in 1943, and a large pilot unit was built by the League in late 1944. All phases of the process were researched by the group for the purpose of developing new ideas and improving existing unit operations. Continuous operation of the pilot unit constructed at the



***Hot spent sulphite liquors from pulp mill are stored in wooden blend tanks***

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**Table II. Production of Sulphite Pulp in the United States[a]**

| *Year* | *Tons* |
|---|---|
| 1940 | 2,607,789 |
| 1941 | 2,918,780 |
| 1942 | 2,930,272 |
| 1943 | 2,436,502 |
| 1944 | 2,386,149 |
| 1945 | 2,359,731 |
| 1946 | 2,476,468 |
| 1947 | 2,795,962 |
| 1948 | 2,811,216 |
| 1949 | 2,536,284 |
| 1950 | 2,855,825 |

[a] Data are from the Census Bureau, U. S. Department of Commerce.

Interlake Division of the Consolidated Water Power and Paper Co., Appleton, Wis., has been supplemented by engineering studies at various member mills.

Laboratory results were confirmed by the sustained pilot runs indicating the process could be expected to achieve 65 to 75% reduction in the biochemical oxygen demand of the spent sulphite liquor. In the meantime shortage of feed proteins, as a result of World War II, and newly developed demands for vitamin products offered definite promise of sufficient market value of the yeast product to justify the high capital investment and high operating charges. Without such returns the process could not have been expected to be practical as a waste treatment process; this concept still applies and serves as the chief limiting factor on wide scale application in the U. S. pulp industry at the present time.

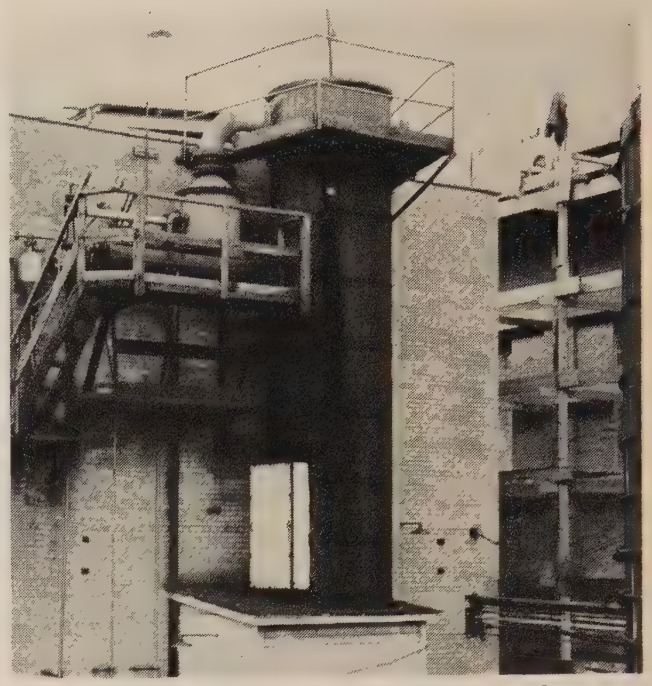
The first commercial feed yeast plant to use spent sulphite liquor in the United States started production in 1948 with an initial design capacity of 4.5 tons of dry yeast daily. This was the Lake States Yeast plant at Rhinelander, Wis., which is described in this article.

## CHEMISTRY AND FERMENTATION MECHANISMS

Table I shows the approximate concentrations of sugars in waste liquors; actually the total solids in spent liquors range from 60 to 150 grams per liter. The composition is subject to some variation due to the kind of wood used and the method and degree of cooking in the pulping process. Hardwood has a higher proportion of pentose sugar. The kinds of sugar are also a function of the wood used, and softwoods have been found to give a product of total sugar running about 70% hexose, largely mannose. Beech and poplar may have as much as 70% pentose sugars, largely in the form of xylose. A larger content of acetic acid is also found in liquors from hardwood pulping.

Mannose and xylose are both good carbon sources for the growth of *Torulopsis utilis*, but the xylose tends to be more difficult to attack and the yields are lower (more carbon dioxide and heat are given off). Hexose sugars are fermented more easily than the pentose sugars and may be selectively fermented in the presence of an abundance of both. The organism must be kept on a controlled feed to prevent an excess of hexoses building up, if the pentoses are to be fermented. Pentoses are not utilized in the alcoholic fermentation by *Saccharomyces* yeasts.

The complex reactions by which sugars, nitrogen, phosphorus, potassium, and minor trace elements are converted by yeast to new cell substance are not as well understood as those involved in the mechanism of



***Sulphur dioxide is removed from feed liquor by steam stripping in this column***

alcoholic fermentation. However, according to Schmidt (*10*), the sugars first undergo a phosphorylation and splitting to three-carbon compounds and thereafter to two-carbon compounds, such as ethyl alcohol, acetic acid, and acetaldehyde:

$C_6$-stage: $C_6H_{12}O_6 + 2H_3PO_4 \rightarrow C_6H_{11}O_6(PO_3H_2)_2 + H_2O$ (1)
Sugar diphosphate

$C_3$-stage: $C_6H_{11}O_6(PO_3H_2)_2 \rightarrow 2C_3H_5O_3 \cdot PO_3H_2$
Phosphoglyceraldehyde

$C_3H_5O_3 \cdot PO_3H_2 + O \rightarrow CH_3COCOOH + H_3PO_4$ (2)
Pyruvic acid

$C_2$-stage: $CH_3COCOOH \rightarrow CH_3CHO + CO_2$ (3)
Acetaldehyde

These reactions are believed to be reversed for the synthesis of new carbohydrate cell material. The two-carbon compounds such as acetic acid, ethylalcohol, and acetaldehyde are each suitable for complete yeast growth. Amino acids, fats, enzymes, and other carbon-containing cellular components are also capable

**Table III. Analysis of Torula Yeast Produced Commercially from Spent Sulphite Liquor**
(All Data on As-received Basis)

| | *Chemical analysis, %* |
|---|---|
| Moisture, atmospheric drying, 2 hours at 105°C. | 5.85 |
| Ash | 9.07 |
| Phosphorus, as P | 1.92 |
| Calcium, as Ca | 0.85 |
| Crude protein (N × 6.25) | 47.43 |
| Crude fat | |
| Standard method | 1.01 |
| With prehydrolysis | 4.84 |
| Crude fiber, with HCl prehydrolysis | 0.82 |

| | *Vitamin assays, γ/gram* |
|---|---|
| Thiamine | 5.3 |
| Riboflavin | 45.0 |
| Pyridoxine hydrochloride | 33.4 |
| Pantothenic acid | 37.2 |
| Biotin | 2.3 |
| Niacin | 417.3 |
| Folic acid | 21.5 |

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of being synthesized from these original two-carbon compounds.

### *Nutritive Value of Torula Yeast*

The yeast produced by the fermentation of spent sulphite liquors is a high protein and high vitamin product. An analysis of the torula yeast produced of the Lake States plant is shown in Table III.

Campbell and Ringrose (*2*, *7*) have made extensive feeding tests on poultry using the torula yeast. It was their conclusion that the yeast could be used as a source of protein for growing chicks and laying pullets and that it was a good source of riboflavin and pantothenic acid. They found no differences in the nutritive value between torula yeast and brewers' yeast when fed in rations with or without animal protein.

Wiley, Dubey, Lueck, and Hughes (*12*) have reported chemical analyses and vitamin assays on samples of the dry torula-type yeast. In general, they found that samples produced commercially from sulphite liquor were uniform in chemical characteristics and in content of various components of the vitamin B complex.

The protein content of torula yeast constitutes about half its total weight, and the yeast compares favorably with milk and meat in amino acid composition. A typical amino acid assay of torula yeast is given in Table IV.

In a series of rat feeding tests at the Forest Products Laboratory, Harris, Hajny, and Johnson (*3*) compared the torula-type yeast with casein as a source of protein. When the rat diet was supplemented with methionine, they found that growth characteristics were comparable with those observed when the rats were fed the casein diet. However, without additional methionine, they reported that the gain in weight of the rats fed torula yeast was only 60% of that for the casein.

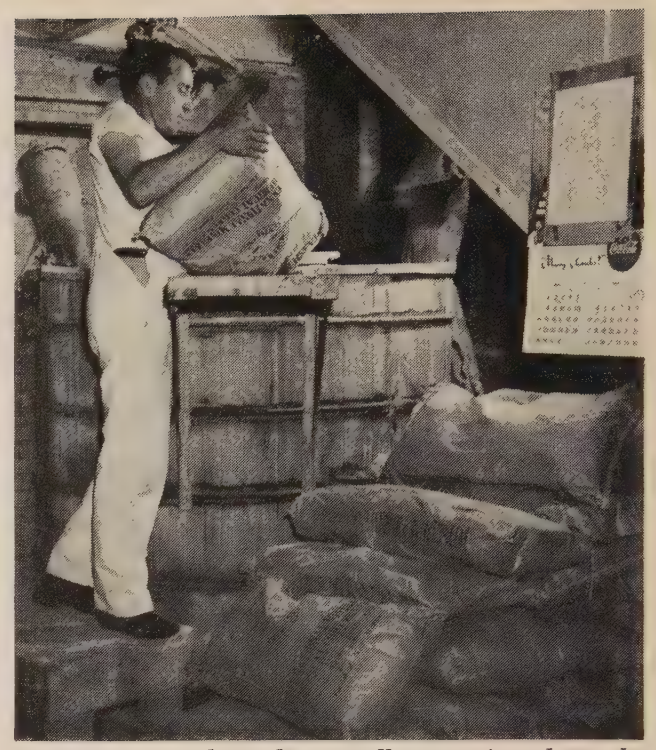
At the present time the principal outlet of the torula yeast produced commercially by Lake States is to the feed supplement industry. Approximately 50 pounds of yeast per ton of feed is the normal recommendation for mixed poultry feeds.

The potential market for feed supplements is very large, ranging into millions of tons annually; the exact figure depends to some extent on who does the estimating. The actual supplement market is growing with increasing knowledge of nutrition being gained on the research and practical levels, and even if the sulphite pulp industry could exploit its potential of 250,000 to 300,000 tons of yeast production annually, this would be only a small portion of the total demand. However, the competitive picture is very complex because of the many other products in the field in large volume.

**Table IV. Typical Amino Acid Assay of Torula Yeast**[a]

| | % *in yeast*[a] |
|---|---|
| Arginine | 3.61 |
| Cystine | 0.68 |
| Glycine | 0.22 |
| Histidine | 1.31 |
| Isoleucine | 3.75 |
| Leucine | 3.57 |
| Lysine | 4.14 |
| Methionine | 0.84 |
| Phenylalanine | 2.41 |
| Threonine | 2.58 |
| Tryptophane | 0.66 |
| Valine | 2.98 |
| Glutamic acid | 6.90 |

[a] All results reported on basis of torula yeast as received.



*Ingredients are charged manually to agitated wooden nutrient mix tank*

Dry torula yeast has been accepted officially or tentatively as a wholesome food and feed material by regulatory organizations in this and other countries. Investigation is now being carried out at several universities with the object of further establishing the nutritive value of torula yeast as a human and animal food.

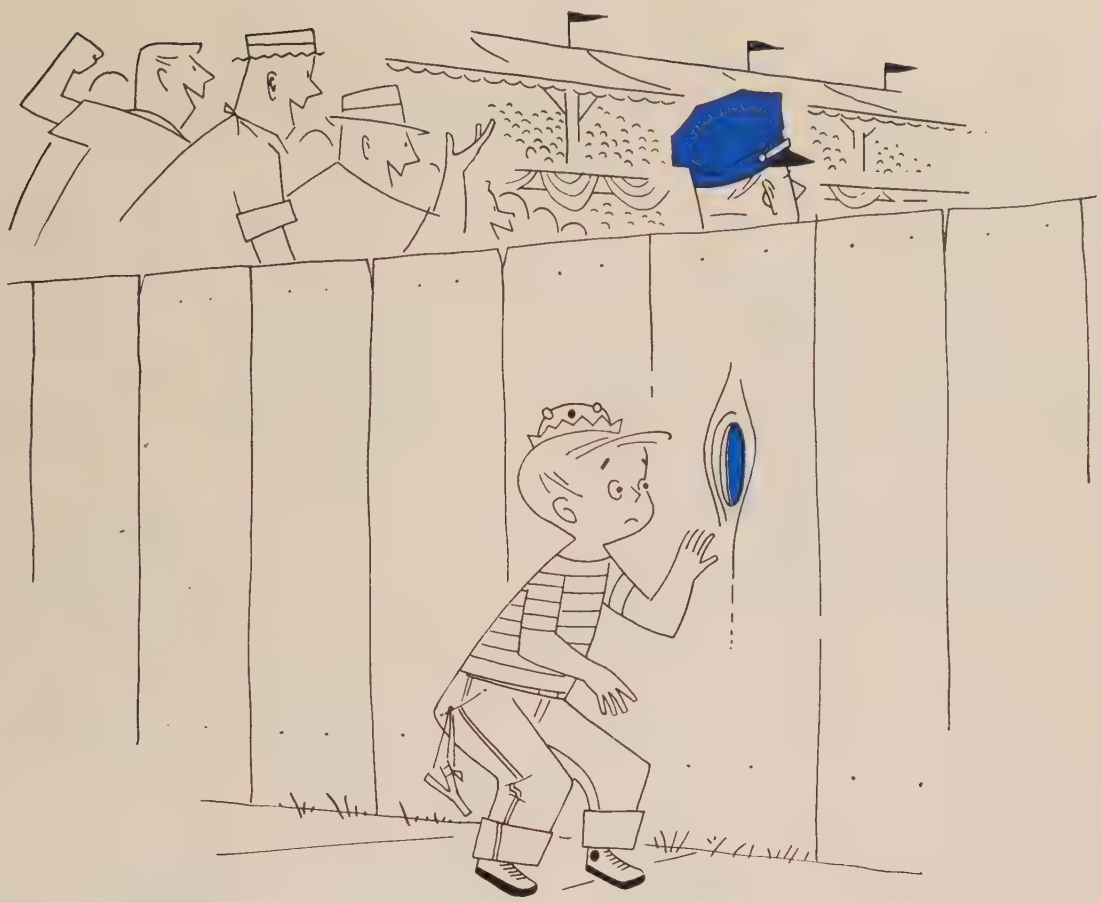
## RHINELANDER, WIS., PLANT OF LAKE STATES YEAST CORP.

The new plant of the Lake States Yeast Corp. is situated adjacent to the sulphite mill of the Rhinelander Paper Co. Waste sulphite liquor from the blow pits in the pulp mill passes through a 6-inch stainless steel pipeline on to a screen and thence into surge or blend tanks. The screen is 80-mesh stainless steel supported by a wooden frame. Corrosion was a problem at the Lake States plant. Materials of construction described in more detail later in this article were selected only after careful study.

Small amounts of wood pulp are retained on the screen and removed manually at approximately daily intervals. The pulp is returned to the stock tanks in the mill for reprocessing. Figure 1 is a flow sheet for the Lake States process.

### *Preparation of Feed Liquor*

Two blend tanks are provided, each with a capacity of 125,000 gallons. One is constructed of 6 by 6-inch and the other of 6 by 4-inch fir staves. Flow from the screen can be directed into either or both of the blend tanks. The tanks are 30 feet in diameter and 26 feet high and are not agitated. A surge capacity this large is important to the process in order to minimize the



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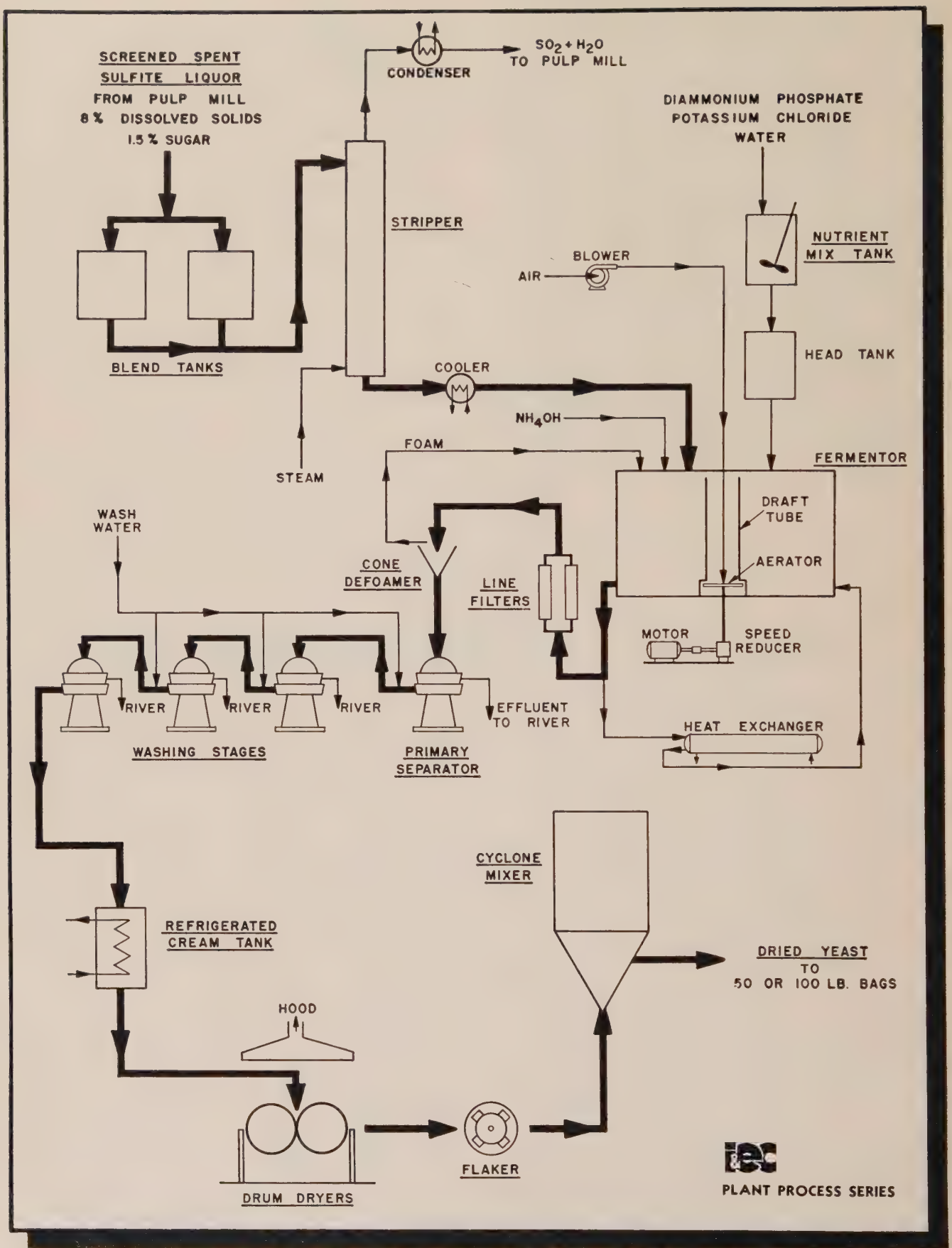


*Fig. 1. Flow sheet for production of food yeasts from sulphite liquors at the Rhinelander, Wis., plant of Lake States Yeast Corp.*

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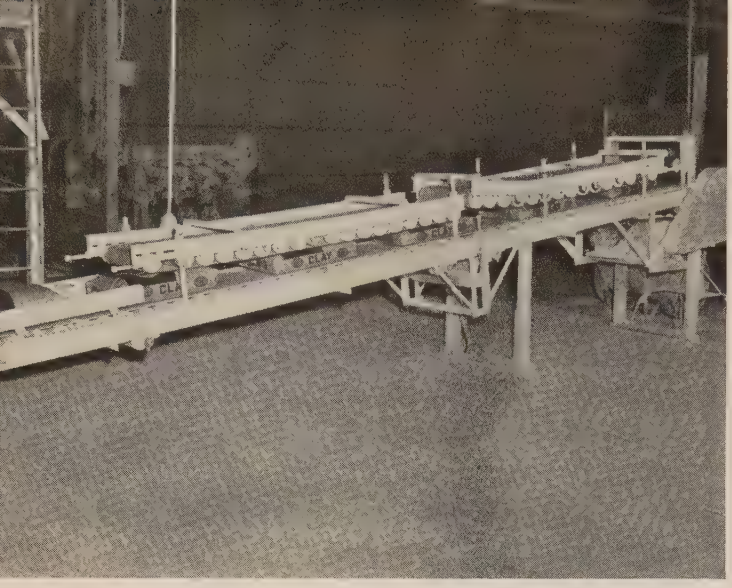

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**WOODEN PALLETS** are usually single-faced, but come double-faced for tiering: single-faced on floor, double-faced above.

**UNLOADING** is almost entirely mechanical with Huber Unit Loads. See customer reactions, right.

**UNIT LOADS** are stacked with de-aired bags. Normal weight per load is 1½ tons. Load base is wooden pallet, at small charge, or fibreboard—both 42″ x 48″.

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age space. Huber does this by de-airing the bags and offering loads on fibreboard sheets or wooden pallets—Huber "firsts" in each case.

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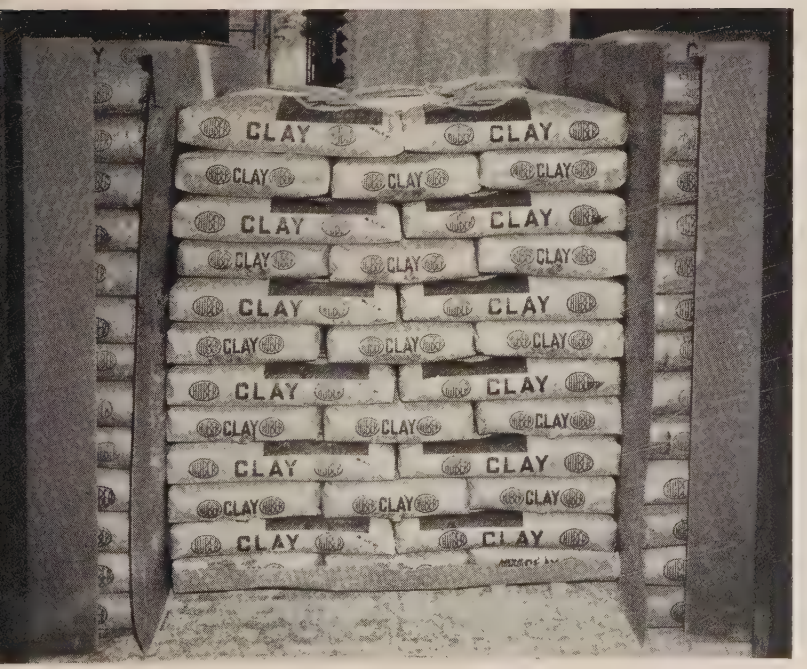



**CAR READY FOR SHIPMENT:** Note fibreboard sheet separators which prevent chafing and bag interlocking.

### TYPICAL CUSTOMER REACTIONS:

"Our saving in unloading time was considerable —about 7.5 man hours. The 400 loose bags in the car center required 6 man hours unloading time, and the 800 bags or 20 unit loads (10 in each end of the car) of 2000 lbs. each required 4.5 hours. This total of 10.5 man hours compares with 18 man hours for a regularly-loaded 60,000 lb. car. In elapsed time, the car was unloaded in 4 hours, with another 1.5 hours for one man storing and decking, as compared to the usual 6 hours—thereby freeing the car 2 hours sooner. This unit loading is a big improvement in handling."

• • •

"We appreciate your cooperation and want you to know that your shipments are coming through in good shape; in fact, better than any other supplier that we have had to date."

### REPORTS FROM AGENTS:

"I have checked with Mr. — and he told me that they unloaded the last car in 2 man hours as compared to 4.5 man hours on the previous one. Breakage consisted of a minor break in one bag. When I spoke with Mr. —, believe me he was tickled pink with the shape the car came in."

• • •

"Mr. — brought up the subject of packaging and praised ours very highly. He said our clay is the neatest, best-stacking material they buy; and it is really appreciated."

• • •

"Mr. — reported that the palletized car which we shipped them recently had arrived in exceptionally good condition and they were very well pleased with it:

(1) Palletized shipments would release a lift truck for further work at the end of approximately 1 hour whereas a shipment of clay by the conventional bag method (*i.e.*, loose bags to their pallets) would tie up a lift truck from 5 to 6 hours.

(2) The fact that they can get a car empty and out of the way in approximately 1 hour, as compared to 5 or 6 hours for a shipment in individual bags, is likewise of value to them."

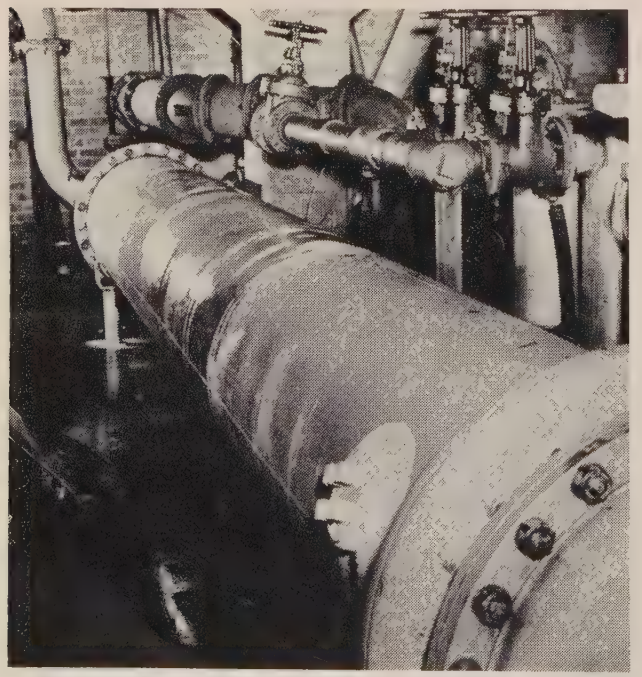
effect of changes in the composition of the liquor from the mill on the yeast fermentation.

The Rhinelander Paper Co., as is the case with many pulp mills, produces several types of pulp from different woods, by different degrees of cooking, and by three different pulping processes (Mitscherlich, direct, and indirect quick cooks). The amount of sugar produced from hemlock and balsam woods is much less than that from spruce, and the liquors have different fermentation characteristics. The large storage and blending facilities serve to level off the sugar load in the feed liquor.

The spent sulphite liquor comes from the pulp mill intermittently at a rate of approximately 125,000 gallons per day. The fermentable sugar content of the liquor averages about 1.5% (approximately 80% hexose and 20% pentose), and the dissolved solids average approximately 8%. Temperature of the liquor is about 170°F., and the pH averages 2.5.

The hot sulphite liquor from the blend tanks is centrifugally pumped to a stripping still at a rate of 100 gallons per minute. The purpose of the stripper is to reduce the sulphur dioxide content of the liquor. The sulphur dioxide exists in a number of forms including total inorganic (sometimes called "free"), organic loosely combined, and firmly bound. The sulphur dioxide bound with lignin in the sulphone form is not of direct concern in the fermentation process and is not readily removed. The sulphur dioxide existing as sulphurous acid or simple salts of inorganic bases and that loosely bound with organics does inhibit yeast growth. German practice involved lime neutralization, but steam stripping has been found more suitable for the conditions at Rhinelander.

The stripper is of stainless steel construction, 5 feet in diameter and 22 feet high. It is packed with Karbate (impervious carbon) 1 by 1-inch Raschig rings. The feed liquor comes in at the top, and live steam enters the bottom of the column through a sparge tube drilled with $22^3/_8$-inch diameter holes. The sulphur dioxide and water vapors pass through a stainless steel spiral-type surface condenser (*1E*), and the condensate is returned to the paper mill for reuse in the sulphite operation. The sulphur dioxide content of this condensate amounts to 8 to 10 grams per liter and represents an important sulphur conservation measure.



***Shell-and-tube heat exchanger for cooling fermenting liquor***

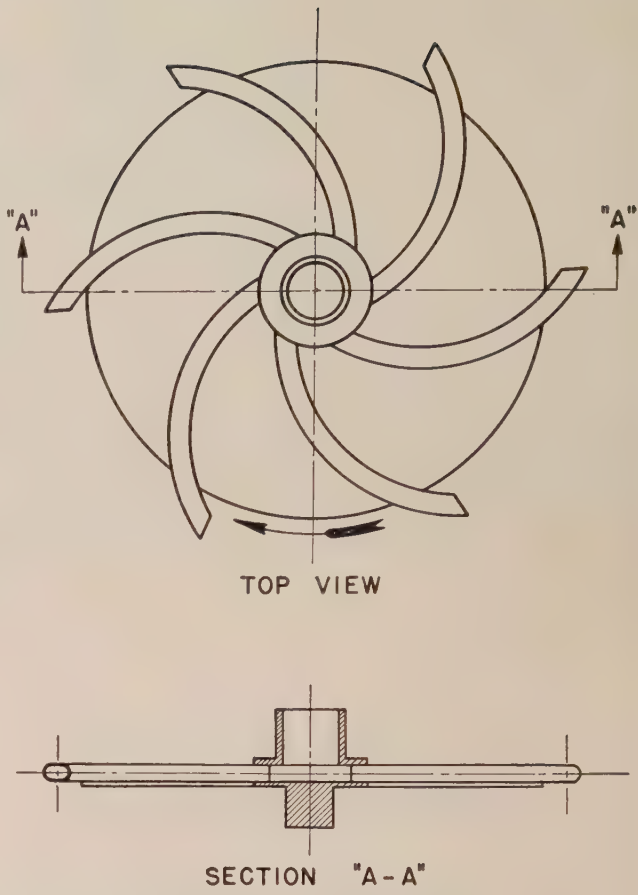



***Fig. 2. Principle of the Waldhof aeration wheel***

Modification of this type aerator is used in the yeast fermentor at Lake States Yeast Corp.

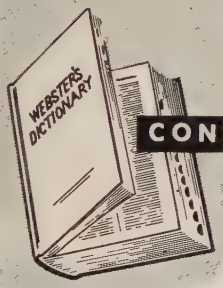
### *Fermentation*

The stripped liquor leaves the bottom of the still column through an automatic level control valve (*8E*) at 180°F. and passes through a stainless steel spiral cooler (*2E*) entering the fermentor at approximately 80°F.

The fermentor is of carbon steel construction, clad with type 304 stainless steel. It is an open-top vessel, 26 feet in diameter and 14 feet high, provided with a center draft tube 4 feet in diameter. The draft tube is supported by means of tie rods attached to the fermentor walls. Operating volume of the fermentor is 45,000 gallons of emulsion (liquor plus entrained air) or some 20,000 gallons of liquor without air. This provides a holding time of approximately 4 hours in the fermentor.

Air is introduced into the fermentor through a rotating pinwheellike aerator composed of open-end tubes rotating at 300 r.p.m. The aerator is driven by a 250-hp. motor provided with hydraulic coupling and speed reducer and connected by means of a shaft through a packing gland on the bottom of the fermentor.

The aerator in use at Rhinelander is a modification of the original German design used by Zellstofffabrik

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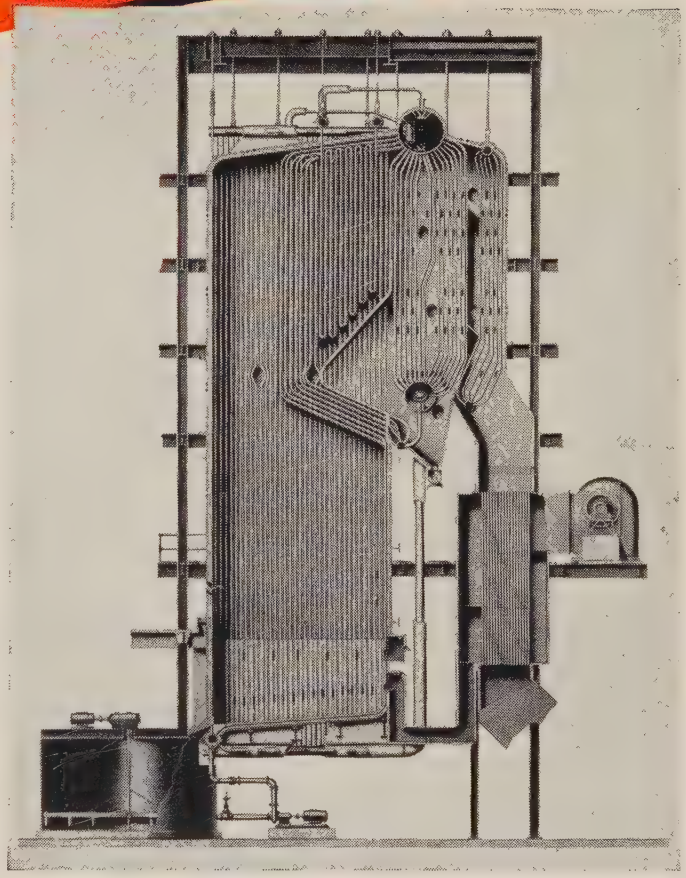

Typical B&W Black Liquor Recovery Unit.

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P-762

Waldhof. The German aeration system has been described in detail by Kiefer (*6*), and the wheel is illustrated in Fig. 2. This general type of aerator design has also been incorporated in the pilot plant fermentor in use at Forest Products Laboratory. Saeman (*8*) has described this installation.

The air is supplied by a single-stage centrifugal blower (*4E*) having a capacity of 1700 cubic feet per minute; the blower is connected to the aerator by means of an 8-inch pipeline down through the center of the draft tube. It is not necessary to sterilize the air prior to use in the fermentation. The aerator serves not only as a means of supplying air but also as a liquor recirculation pump. The combination of this type aerator with the draft tube makes the addition of an antifoam agent unnecessary. The air flow is controlled manually by a butterfly valve on the suction side of the blower. The flow rate is measured by means of a standard orifice and water manometer tube setup. Once the fermentation is under way, only minor changes in the air flow are required.

Diammonium phosphate and potassium chloride are made up in a water solution in a 500-gallon wooden mix tank and pumped to a surge tank located above the fermentor. The mix tank is provided with a top-entering agitator (*10E*). Although the nutrient mixing is a batch process, the feed to the fermentor from the surge tanks is continuous and by gravity.

Anhydrous liquid ammonia is received by tank car and made into an aqueous solution to a concentration of approximately 20% ammonia. This ammonia solution is fed continuously to the fermentor at rates based on the sugar content of the feed liquor. The rate is manually controlled and indicated by a rotameter. The pH of the fermentation mixture (wort) runs about 5.0.

The stripped liquor, nutrients, and ammonia all enter the fermentor at or near the top of the draft tube. The flow through the tube is down, and this arrangement provides the most rapid mixing.

The temperature of the fermentation is controlled at 37°C. by circulating the wort through a shell-and-tube heat exchanger at the rate of 1500 gallons per minute. Using spruce spent sulphite liquor, 3750 calories of heat are evolved per gram of dry yeast produced. Liquors from hardwoods, high in pentose sugars, increase the cooling requirements. In Germany it was found that yeast production from beechwood liquor evolves 4600 calories per gram of dry yeast produced.

The wort is taken out of the bottom of the fermentor on one side and pumped to the bottom of the fermentor on the other side. Additional cooling, for use during the warm seasons, is provided by a water spray ring around the outside upper edge of the fermentor. The water is collected in a trough welded to the lower part of the fermentor.

The fermentation is continuous, and after an initial inoculation with the laboratory culture of *T. utilis* no further inoculations are required.

The yeast fermentation has been remarkably free from contamination. In more than 2 years of operation of the Lake States plant, production has never been interrupted because of contamination. The conditions of pH, temperature, and aeration with agitation permit the propagation of *T. utilis* at rates rapid enough to overgrow and prevent the development of foreign organisms.

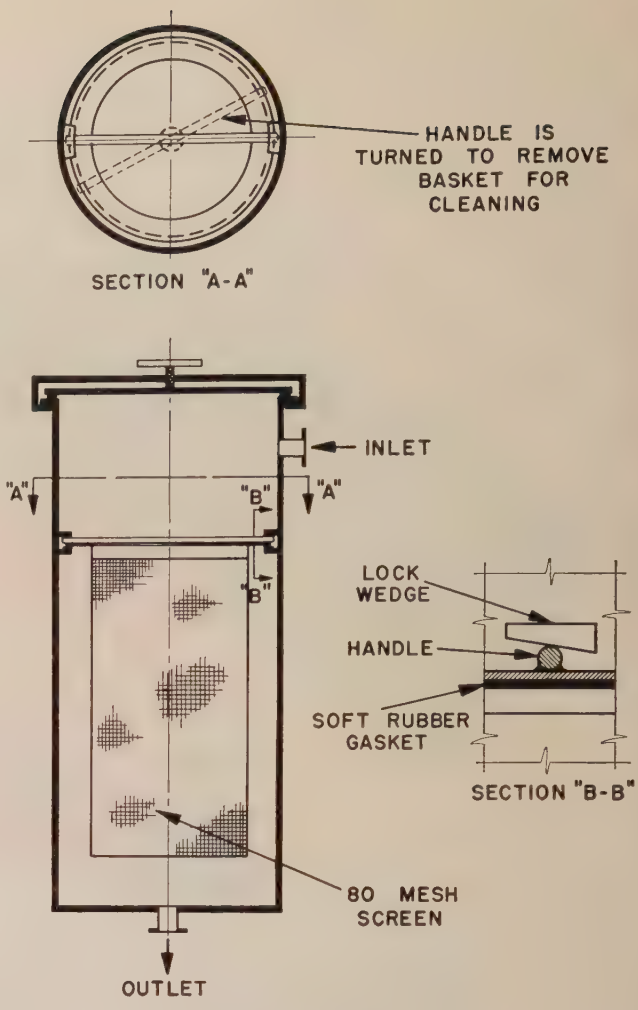


***Fig. 3. Cross section of line filter used to clarify feed to yeast separators***

Filter was designed and built by Lake States Organization

### *Yeast Separation*

A side stream from the inlet to the fermentor heat exchanger is taken off at a rate equivalent to the total fermentor feed. This flow is manually controlled to maintain a constant level in the fermentor. The stream passes through two screen-type line filters (Fig. 3) situated in parallel and then to a cone located above the open head of the fermentor. One of the filters can be taken off the line for cleaning without interruption of the operation.

The cone serves as a foam separator. Foam overflowing from the top of the cone is recovered in the fermentor. The liquor-yeast emulsion is taken from the bottom of the cone and flows by gravity to a centrifugal separator (*7E*). The aqueous solution is lighter than the yeast, and separation by centrifugation is relatively easy. The purpose of this primary separation is to get rid of as much of the liquor as possible. The relatively sugar-free separator effluent is discharged to the river.

The cream containing the yeast from the primary separator is collected in a cream trough and pumped to washing stage separators. Well water is used for washing and is pumped into the separator feed. The

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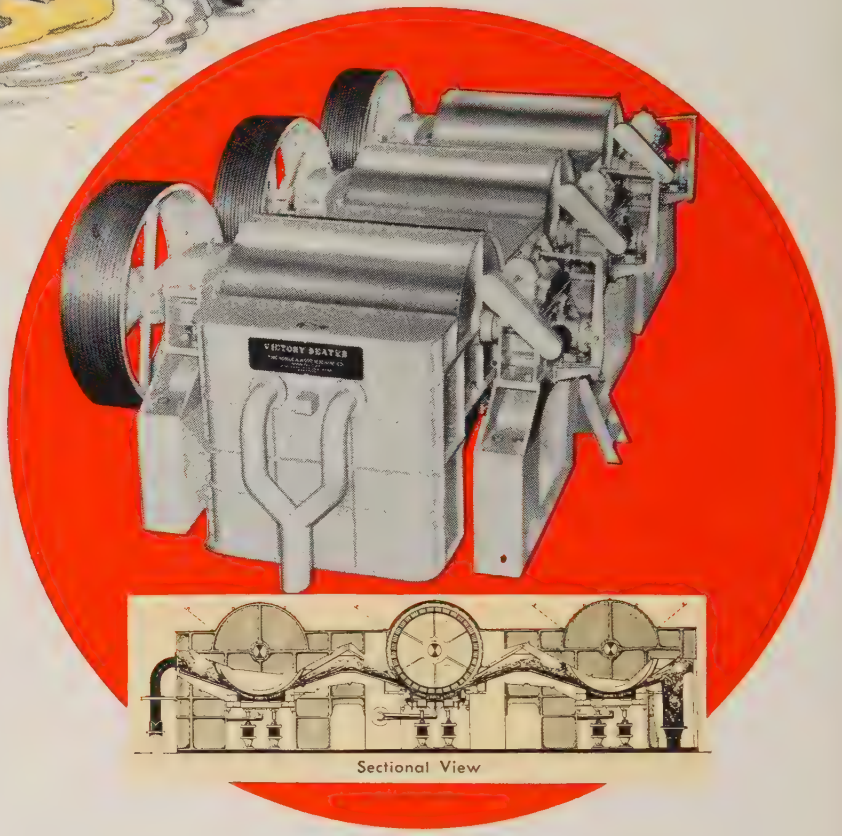


Sectional View

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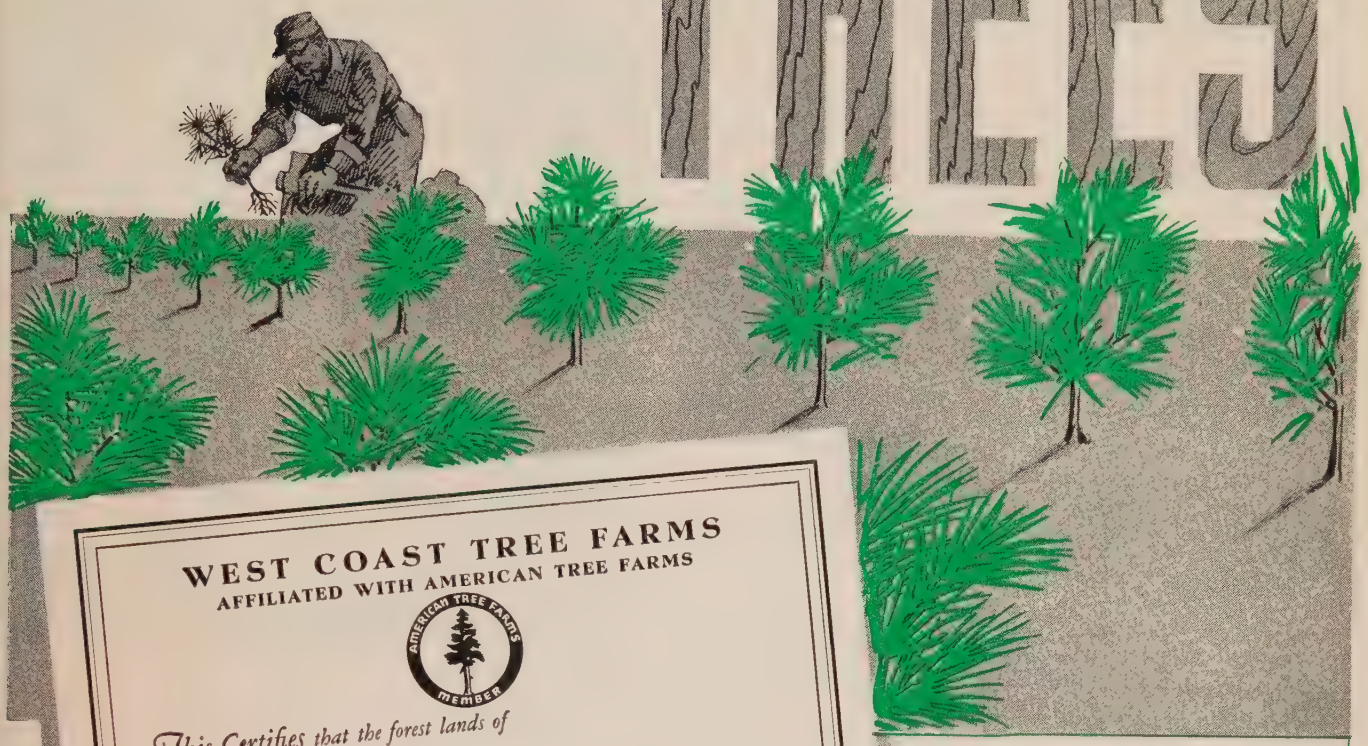

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*This Certifies that the forest lands of*

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*Chairman, Joint Committee on Forest Conservation*

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10. **Calapooya**
11. **Millicoma**
12. **Klamath Falls**
13. **Skykomish**
14. **Copper Creek**

PULP DIVISION **WEYERHAEUSER**

water layer from each washer is discharged to the river, and the cream is pumped to the following stage.

This washing operation is repeated in three stages. The effluent going to the river from the primary separator has an average fermentable sugar content of 0.2% compared with the 1.5% sugar in the fermentor feed liquor. The biochemical oxygen demand of the liquor processed is reduced approximately 65% by the operation.

The yeast concentration in the fermented wort to the centrifuges is about 1% on dry basis, and the primary stage concentrates amount to 10 to 12% solids. Subsequent washing steps give a cream to the drier with 14 to 18% yeast solids.

Cream from the final washing stage is discharged to an agitated storage tank. This cream tank is insulated with 4-inch magnesia blocks and provided with coils connected to a conventional liquid ammonia refrigeration (*11E*); capacity of the tank is 1000 gallons. The cream tank is refrigerated only during periods when the fermentor is not in operation. If the fermentor is emptied, the cream tank is held under refrigeration and its contents are used as inoculum to start the fermentation again.

Yeast from the cream tank is pumped to twin drum rotary driers (*5E*) of cast-iron construction. The drums, 42 feet in diameter and 120 feet long, are heated by steam under 80 pounds pressure. Vapors from the drying operation are collected by a hood over the drums and discharged to the atmosphere through a stack.

The dried yeast coming from the hot drums falls into a trough containing a screw conveyor (*6E*). It is then transferred by a bucket elevator to a flaker (*6E*). The flaker is a hammer mill type arrangement consisting of a cylindrical screen with rotating internal blades.

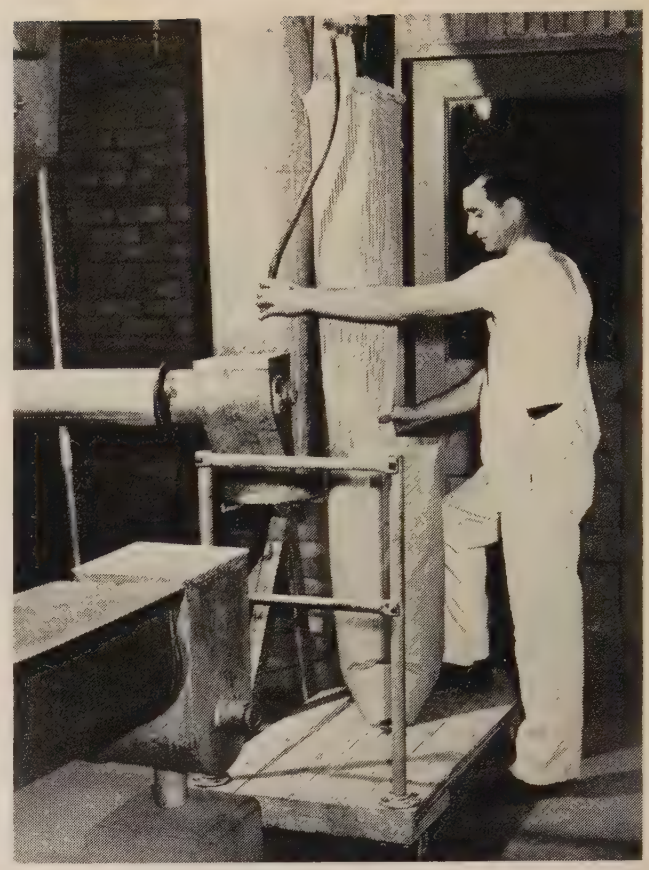
The flaked yeast passes to a screw conveyor which discharges inside a cyclone mixer (*3E*). The mixer is similar in design to the conventional cyclone dust collector. The yeast is bagged from the cyclone mixer into 50- or 100-pound multiwalled paper bags. The product is nonviable and has an average moisture content of about 6%.

As with most industrial fermentations, operation is on a 24-hour basis, with shutdowns only in emergencies. The operating crews work in 6-hour shifts for a total work week of 36 hours. There are three operators on each shift, plus a small maintenance crew working only the day shifts. The control testing in the laboratory is done by the chief chemist.

## CHEMICAL CONTROL

Depending on the complexity of the test or the need for immediate results, chemical analyses of the process samples are carried out by the nontechnical operating personnel, the plant chemist, or the research group of the Sulphite Pulp Manufacturers' Research League.

The nutrient feed rates are regulated according to a quick sugar test run by the plant operators. Relative values for residual sugars are determined once each shift or oftener by rapid titration based on the Soxhlet method of sugar analysis. Results are available within a few minutes and serve as a quick guide for adjustment of the feed rates. However, because of the presence of



***Dried yeast from cyclone mixer is packaged in 50- or 100-pound bags***

variable amounts of other reducing substances, this test requires confirmation by at least daily checks using the more accurate but slower method in the chemical laboratory.

A simple centrifuge test for measurement of wet yeast volume in the fermentor is run under standardized conditions each hour. In this test a measured volume of defoamed wort is placed in Hopkins' vaccine centrifuge tubes and spun at 2000 r.p.m. for exactly 10 minutes. Under conditions of continuous yeast growth, this test provides a sensitive method of measuring the state of growth in the fermentor. Similar tests are run on samples from the separators as an indication of the efficiency of the yeast separating and washing steps.

In the chemical laboratory a complete sugar analysis is run each day as a check on the quick sugar test run by the operators. The more accurate method is based on use of a modification of the semimicro method of Somogyi on samples which have first been treated to remove lignin and other nonsugar reducing substances. In the chemical laboratory checks are also run each day on the Kjeldahl nitrogen analyses which are made twice each shift by the operators. Daily composites, based on hourly samples of raw, stripped feed, and centrifuge effluent liquors, are used for a check on the 5-day B.O.D. removal efficiency of the yeast plant.

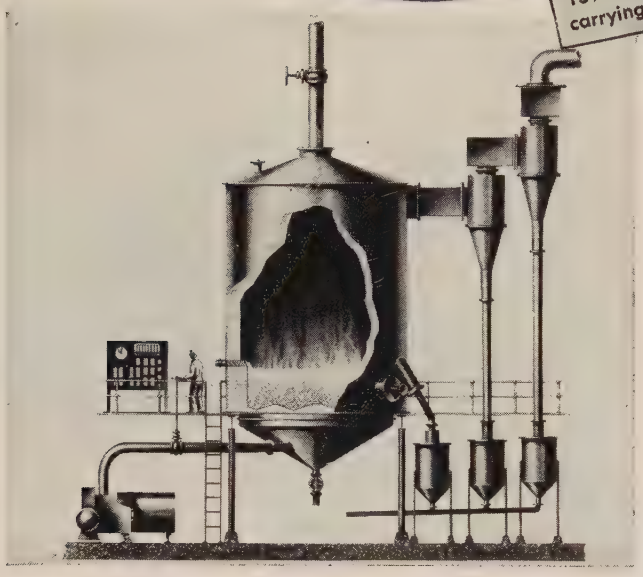
The chemical laboratory determines moisture content by oven-drying on samples taken from each 1000-pound lot as produced. Periodic checks of phosphorus and ash content of the final product are also carried out using A.O.A.C. methods.

The Appleton laboratory of the Research League has taken care of the more complicated control tests for vitamins. Duplicates of all yeast samples and

# Can you use 14-15% $SO_2$ GAS from PYRITE

***Dorrco FluoSolids* will produce it . . . at lower investment and operating costs than conventional roasters.***

**FACTS ON $SO_2$ PRODUCTION BY FLUOSOLIDS**



**GAS STRENGTH** will average 14-15% $SO_2$ dry basis from pyrite carrying 48-50% sulphur.

**GAS CLEANING EQUIPMENT** is smaller because of smaller gas volumes.

**FEED** can be relatively coarse . . . flotation concentrate to 35 mesh—jig or table concentrate to 14 mesh.

**MINIMUM MAINTENANCE** . . . no moving parts exposed to high temperature — long refractory life.

**NO SCALING** . . . temperature accurately controlled below fusion point.

**NO EXTRANEOUS FUEL** is needed once fluidized bed is up to calcining temperature.

**PROCESS SHUT-DOWNS** of two or three days present no roasting problem.

**COMPLETE INSTRUMENTATION** eliminates the personal factor in operation.

● Sulphuric acid manufacturers and all users of sulphur dioxide faced with a shortage of elemental sulphur will find in FluoSolids an economically feasible means of tapping sulphides as an alternate source of $SO_2$. Utilizing the principle of fluidization, The Dorrco FluoSolids System is a distinct departure from conventional roasters. It brings $SO_2$ production from those sources down to a reasonable investment and operating cost level.

Its economy, simplicity and ease of operation are indicated by the facts above. For more detailed information write to The Dorr Company, Stamford, Conn., or in Canada, The Dorr Company, 80 Richmond Street West, Toronto 1.

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composites are forwarded there. However, at the present time a new spectrophotometer is being set up at the Rhinelander plant.

The spectrophotometer is primarily a research instrument to be used for developing colorimetric, turbidimetric, and fluorometric analyses in close cooperation with the Appleton laboratory which is already so equipped. Simpler control instruments may be used eventually. Elemental analyses on the nutrients and substrates, new methods for turbidimetric control of yeast concentrations, and vitamin assays by various standard techniques may be made.

Practically all control tests for the yeast process were originally developed or adapted by the research staff, and this is also true of the vitamin assays and more complicated chemical testings. Table III indicates the chemical analyses and vitamin assays carried out on samples of the complex yeast product.

Samples are taken from every tenth 100-pound bag of yeast or twentieth 50-pound bag—that is, every 1000 pounds—in accordance with standard sampling techniques of the A.O.A.C. and the American Association of Feed Control Officials.

## MATERIALS OF CONSTRUCTION

An extensive program of testing corrosion resisting alloys, coatings, and other construction materials led to adoption of type 316 or 317 stainless alloys for all piping, pumps, and metal surfaces in contact with the raw feed liquor up to and including the stripper equipment. The stripped feed liquor, after removal of sulphur dioxide, can apparently he handled without difficulty by types 302, 304, and 416 stainless alloys through the fermentor, emulsion cooler, and centrifuges. Baked-on Heresite phenolic-base coatings (*9E*) have been found excellent for yeast holding tanks in both the pilot and commercial units. For large liquor storage tanks, fairly good experience has been obtained with 4-inch thick Douglas-fir heartwood tanks.

The fermentor in the Lake States plant is carbon steel clad with type 304 stainless steel. In Germany, where cost and availability were prime factors, wood vats were found to be satisfactory. Newer fermentors in Germany have been constructed with concrete and lined with tile (*9*). Unlined concrete is undesirable because vigorous mechanical aeration and relatively low pH results in sand getting into the product.

The open fermentor with intense aeration leads to prevalence of high humidities on the operating floor. This has been a serious nuisance and causes an accelerated corrosion of piping and destruction of painted surfaces. Plans are currently under way to provide increased ventilating capacity. A similar problem in the drier room was taken care of in the first year of operation by means of appropriately located ventilating ducts.

## EFFLUENT

At the Lake States plant, samples of the feed and effluent liquors are taken each hour and are composited for B.O.D. analysis each 24-hour period. Average data for liquor processed in 1950 show 59.7% reduction in B.O.D. from all samples taken during the year. Monthly averages were improved with changes in processing methods, and a high of 64.5% was achieved during one month's run. Individual 24-hour composites frequently show 70% reduction of B.O.D. in liquor processed by the plant. Pilot plant data have demonstrated possibilities for 75% B.O.D. efficiency by the yeast process, and this serves as a goal for the commercial operation.

***Research work on sulphur dioxide stripping***
Small scale equipment is used by the staff of the Sulphite Pulp Manufacturers' Research League

The remaining 25% of biochemical oxygen demand in the yeast plant effluent apparently results from carbohydrate material derived directly or indirectly from the hydrolytic breakdown of sugars. These products have yet to be fully identified. Numerous attempts to find means for practical biological processing have not been successful, but there is some possibility that this problem will also be solved.

Much speculation has attended the deoxygenating effect of the lignosulphonates present in spent sulphite liquor when disposed to streams and other dilution waters. Latest evidence points to the relative stability of these compounds. Appreciable degrees of lignosulphonate destruction apparently do not take place biologically in less than 20 days, and this slow rate probably does not show up in streams by present methods of measurement.

The Sulphite Pulp Manufacturers' Research League studied the effect on the B.O.D. of the effluent resulting from different degrees of treatment. This is a complex problem and variations are wide. A simplification of present conclusions and observations is summarized in Table V.

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## FUTURE

Research at the present time is directed toward improved aeration, better yeast recovery and washing, more efficient fermentor cooling, and further evaluation of the nutritive value of the yeast product.

The efficiency of aeration, agitation, and mixing in the fermentor are critical to over-all plant efficiency. Development work on this phase has been carried out by the Research League continuously since 1943 and substantial improvements are still believed possible. The power requirements of the method are high.

Much time was devoted to the study and development of the yeast separation and washing. Filtration by various methods, both atmospheric and vacuum, and all types of centrifugal equipment have been investigated. These operations have been carried out both independently and in cooperation with the various equipment manufacturers. At the present time centrifugal equipment (*12E*) of German design is being studied with the hope that efficiency can be improved.

Cooling of the fermentor liquor with its large amount of entrained air is at its very best an inefficient process. As much of the heat as possible is removed from the feed liquor prior to entering the fermentor and the recovery of the heat for use in the pulp mill has been studied but as yet not applied in the present plant.

A number of research fellowships are being maintained at various universities in order that more information may be obtained on the nutritive value of the torula yeast. The yeast is apparently a quite satisfactory human food, and development of this outlet for the product might well change the entire economic picture of the process.

The future of the yeast from spent sulphite liquors seems to be dependent on the degree of success of cost reduction and product promotion efforts. It is now a question of economics more than of fundamental technology.

**Table V. B.O.D. Removal from Spruce Waste Liquors**[a]
(Data are only approximate)

| *Extent of treatment* | *Composition change* | *Residual 5-day B.O.D., mg./liter* | *B.O.D., % removed* |
|---|---|---|---|
| None | Whole liquor | 35,000 | 0 |
| Pretreatment by stripping or precipitation | $SO_2$ removed | 31,500 | 10 |
| Pretreatment and alcoholic fermentation | $SO_2$ and hexose sugars removed | 15,750 | 55 |
| Pretreatment and torula yeast fermentation | $SO_2$ hexose and pentose sugars, and some acetic acid removed | 8,750 | 75 |

[a] 13% solids content (digester strength).

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## PROCESSING EQUIPMENT

(1E) American Heat Reclaiming Corp., New York, N. Y., Spiral heat exchange, Type III.
(2E) American Heat Reclaiming Corp., New York, N. Y., Spiral heat exchange, Type I.
(3E) Brawer Mfg. Co., Quincy, Ill., Whirlwind feed mixer No. 3835V.
(4E) Buffalo Forge Co., Buffalo, N. Y., No. $5^1/_2$ E blower arrangement 4.
(5E) Buffalo Foundry & Machine Co., Buffalo, N. Y., Buflovak roll drier, Series 700.
(6E) Buffalo Foundry & Machine Co., Buffalo, N. Y., Buflovak conveyor, elevator, and flaker unit, 1000 Series.
(7E) DeLaval Separator Co., New York, N. Y., Separator Model ADVK-6.
(8E) Fisher Governor Co., Marshalltown, Iowa, Level control valve, Type 410–50.
(9E) Heresite and Chemical Co., Manitowoc, Wis., Protective coatings.
(10E) Mixing Equipment Co., Rochester, N. Y., Lightin' mixer Model S-2.
(11E) Vilter Mfg. Co., Milwaukee, Wis., Ice machine Ser. No. 249551.
(12E) Westphalia Separator A.G., Westphalia, Germany, Model HFH separator.

Published in the August, 1951, issue of *Industrial and Engineering Chemistry* as a staff-industry collaborative report and reprinted by permission of the editors.

Portions of the Introductory material for this paper have been derived from a chapter on Food and Feed Yeasts written by A. J. Wiley for publication in a new book, "Industrial Fermentations," L. A. Underkoffler, editor, Chemical Publishing Co. (in preparation).

*Early Paris post office. Illustration from Bettmann Archive.*

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Older than paper, far older than printing is the idea of a postal service. It began in primitive Persia, flourished in ancient Rome. Even through the "Dark Ages," Merchant Guilds carried it on. But a King of France, Louis XIV, in 1653 first extended postal service to the individual. For a sou, the Paris post office would deliver a letter to your private abode.

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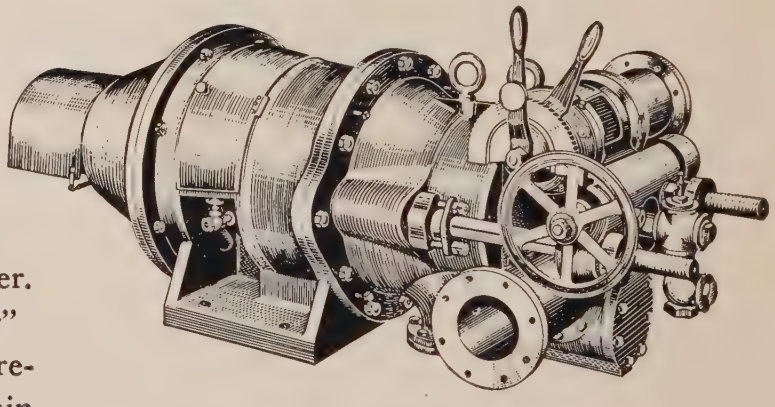

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Left: No. 1 Puseyjones Machine installed at Union Bag in 1936, and No. 2 Puseyjones Machine which went into operation in 1937.

Right: No. 4 Puseyjones Machine installed at Union Bag in 1942 is making liner board for corrugated shipping containers. Just visible at left is the No. 3 Puseyjones Machine which went into operation in 1937.

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No. 5 Puseyjones Machine installed at Union Bag in 1946.

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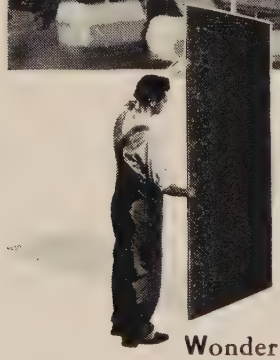

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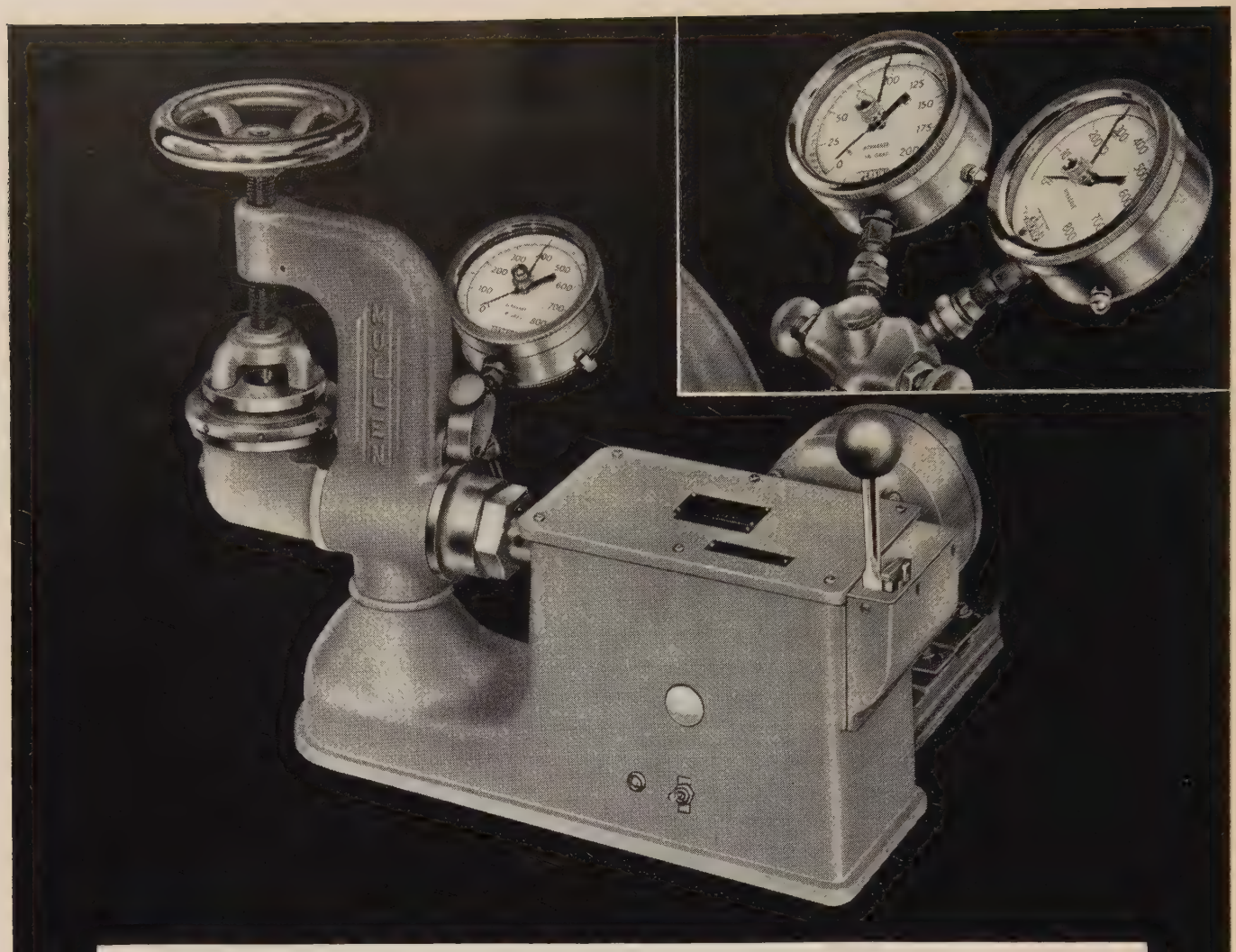

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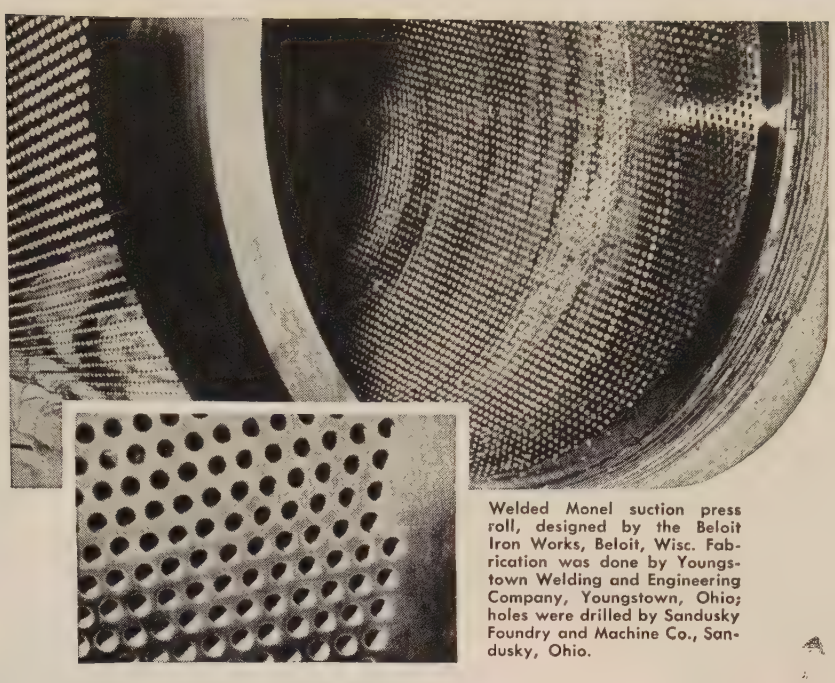

Welded Monel suction press roll, designed by the Beloit Iron Works, Beloit, Wisc. Fabrication was done by Youngstown Welding and Engineering Company, Youngstown, Ohio; holes were drilled by Sandusky Foundry and Machine Co., Sandusky, Ohio.

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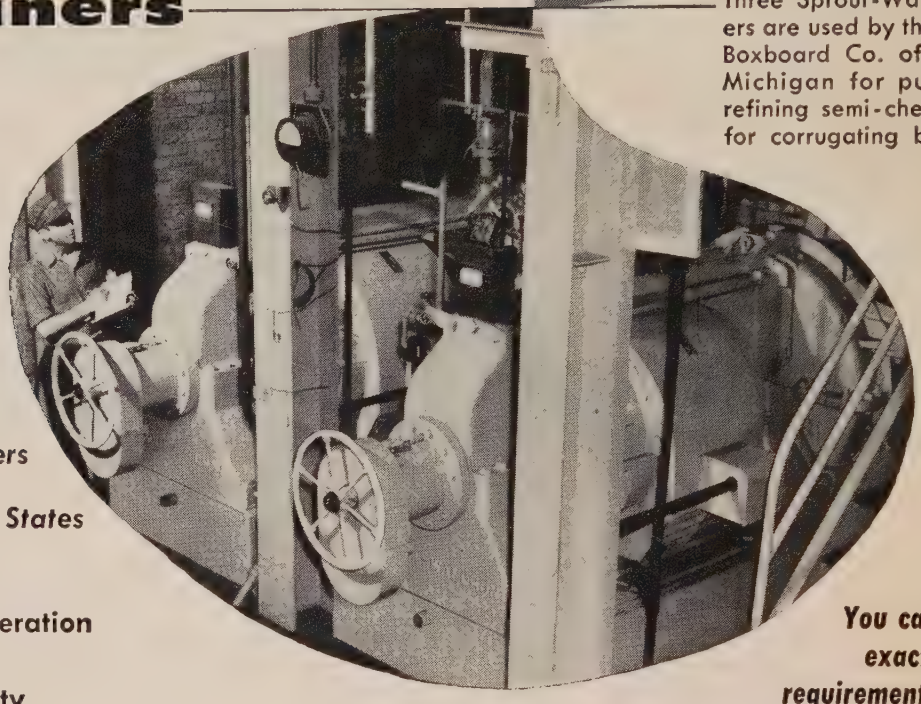

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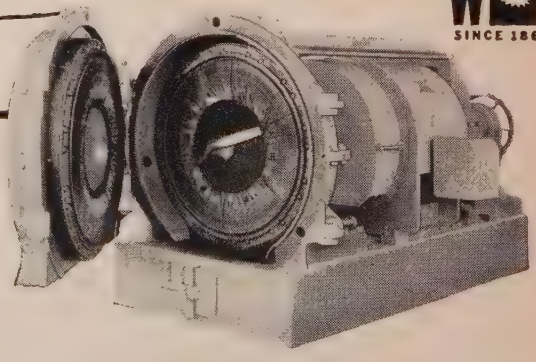

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# The Hercules Print Tester

E. J. BARBER and J. W. DAVIS

**An instrument has been developed for measuring the pick resistance of mineral-coated printing papers. The instrument embodies the basic principles of a printing press. Small strips of the test specimen are printed with an ink-like material under controlled conditions. The speed of printing is increased by small increments until picking of a test strip occurs. Factors affecting test results obtained with the instrument are: (1) speed of printing, (2) ink tack, (3) ink temperature, (4) ink volume, and (5) impression pressure. Speed of printing provides the principal means for varying the stress to which the test sample is subjected. Ink tack can also be varied conveniently to extend the stress range. Ink temperature is held constant. Ink volume and impression pressure are adjusted to produce a good quality solid print on the test strip. An examination of operating variables and a description of operating procedure are included.**

THE need for a simple and reliable prepress method of measuring pick resistance of coated papers has long been recognized. Such a method is essential to effective adjustment and control of adhesive content in the manufacture of coated papers. The use of an excess of adhesive to insure freedom from picking is uneconomical and cannot really be considered a satisfactory approach to the problem of obtaining optimum balance in printing properties (*1*). In the evaluation of experimental adhesive materials, a dependable method of measuring pigment binding power is essential.

In 1941 and 1942 the Institute of Paper Chemistry published a series of reports (*2*, *3*, *4*) entitled, "Determination of Bonding Strength of Paper." These reports described an instrument by which a test specimen could be subjected to a controllable picking stress in a manner similar to that of a printing press. The investigation was followed by the development of at least three pick testing machines (*5*, *6*, *7*). The instrument described in this paper is the outgrowth of a project started in 1944.

In the preliminary stage of our laboratory investigation, the results obtained at the Institute were corroborated using a device of like design. It was then decided to build an instrument similar in principle but different in design in an effort to simplify the test procedure. A description of the new instrument (Fig. 1) and an examination of the various factors affecting its performance are presented below.

The fundamental parts of the new instrument consist of three units: (1) a small rubber inking roller about $^5/_8$ inch in width and $2^1/_2$ inches in diameter; (2) a variable-speed, motor-driven combination printing roller and driving wheel; and (3) a combination driven wheel and impression cylinder which carries the sample (Fig. 2). The first unit is adequately described under (1) above (see Item 1 of Fig. 2). The second unit (2) consists of a polished steel printing roller, $^5/_8$ inch in width and $3^1/_2$ inches in diameter, and a rubber-covered driving wheel of the same dimensions. The third unit (3) in the series consists of a steel wheel, one-half of which has been cut away to the hub, and an impression cylinder sample carrier of the same radius. Two-thirds of the impression cylinder has been cut away to the hub. The remaining arc has flanged and slotted edges (see Fig. 2).

A strip of paper $^7/_8$ by 8 inches is mounted on the impression cylinder and held in position by a clip on the leading end and by the slotted flanges at the edges of the arc over which the sample is drawn. The arc is made of steel, and the test sample is underlaid with packing as in a commercial press. The combination driven wheel and impression cylinder unit is balanced so that, when its catch is released, the unit rotates enough by gravity to bring the driving arc into contact with the rubber-covered wheel of the combined driving and printing roller. The drive wheels are in contact through an arc of 180°. Toward the end of the driving stroke the impression cylinder carries the sample into contact with the printing roller or plate cylinder. The impression cylinder unit is carried through by its momentum and is stopped at the end of one revolution by a friction brake and a triggerlike catch device.

Operation of the instrument proceeds as follows. The temperature of the plate cylinder is read from a special thermometer recessed in the end surface of the plate cylinder (Fig. 2). The bulb end of the thermometer comes within a quarter of an inch of the printing surface of the plate and makes possible the detection of slight changes in the temperature of the cylinder at a point near the printing surface. This temperature can easily be maintained within ±0.2°C. Adjustments are made by warming with the hand or by cooling with a few drops of acetone. Operation of the instrument in a

*Fig. 1. The Hercules print tester*

E. J. BARBER, Research Chemist; and J. W. DAVIS, Supervisor, Paper Makers Chemical Research Division, Experiment Station, Hercules Powder Co., Wilmington, Del.

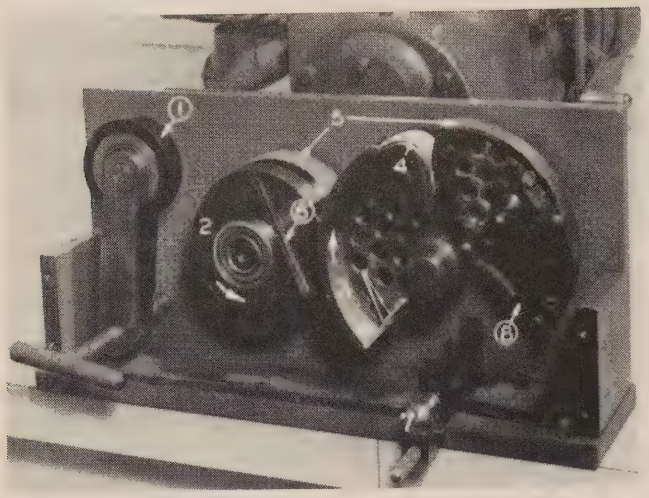

*Fig. 2. Close-up of print tester with end plate off*

(1) Inking roller. (2) Plate cylinder. (3) Impression cylinder ($^3/_4$ way through cycle). (4) Test strip. (5) Driving mechanism. (6) Thermometer. (7) Release and stop device. (8) Brake shoe.

constant-temperature, constant-humidity room is an aid to ink temperature control. However, as in most paper tests, the principal reason for working under standard conditions of temperature and humidity lies in the nature of paper.

After the temperature check a predetermined volume of ink is applied to the surface of the rubber inking roller from a modified 1-cc. hypodermic syringe (Fig. 3). This syringe is equipped with a collar containing an adjustment screw which makes possible the measuring of 20 to 70 mg. of ink with a precision of ±0.5 mg. Following ink application to the inking roller, the plate cylinder is put into motion by starting the electric motor to which it is connected through a cone-type variable-speed transmission. The inking roller is swung into contact with the plate cylinder and slowly oscillated by hand in order to distribute the ink evenly over the surface of the two rollers. Very uniform distribution can be attained within 20 seconds. Then, with the inking roller still in contact with the plate cylinder, the impression cylinder is released and allowed to make one revolution in which the sample is printed. The speed of the printing cycle is determined by the setting of the variable-speed transmission.

The printed strip carrying a $^5/_8$ by $4^1/_2$ inches solid print is then removed from the impression cylinder and examined for cracks or coating picks. A low-power binocular microscope is a valuable aid in examining the printed strip for minute picks and for cracks which usually appear at speeds just below the critical picking speed. In some cases submacroscopic picks may occur over a considerable range of printing speeds before gross

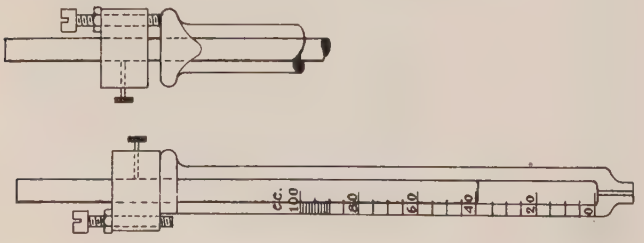

*Fig. 3. Ink syringe*

picking occurs. We believe it is desirable to detect these minute picks because the accumulation of material from such picking would soon foul the plate of a commercial press. The microscope also aids in judging the quality of the print.

The major variables in this process are: (1) speed of printing, (2) ink viscosity or tack, (3) ink temperature, (4) volume or weight of ink used, and (5) impression pressure.

The stress to which the sample is subjected in the printing operation is essentially a product of ink tack and printing speed. These two factors constitute the principal variables in the process and make it possible to vary printing stress over a wide range. Actually, it is preferable to hold ink tack constant and vary only printing speed; however, ink tack can be varied readily at will. For a discussion of ink tack see (*8*).

A wide variety of tacky materials may be used as inks. The IPI series of tack-graded black test inks (*9*) were found to be well-suited to this test. These inks provide an effective means for varying tack under

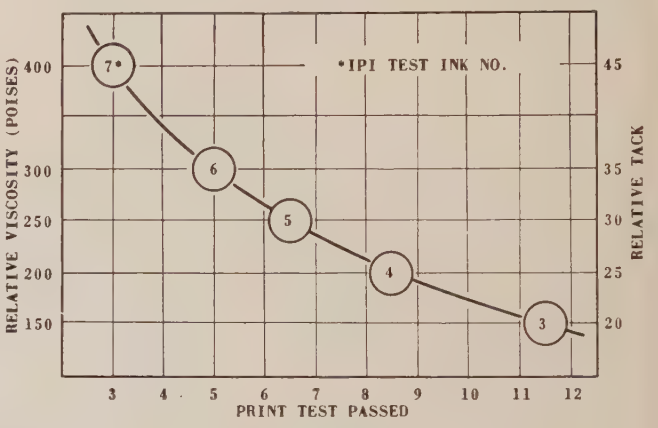


*Fig. 4. Print test passed vs. relative viscosity and tack of IPI tack-graded inks*

(Numbers in circles are the IPI ink numbers)

known conditions, and they yield sharp black prints which simplify the detection of coating cracks and picks. Figure 4 demonstrates the relationship between pick point and the IPI tack-graded inks. For a description of the terms, relative tack and relative viscosity, used in Fig. 4, see (*9, 10*). The print test or pick point values shown in Fig. 4 and elsewhere are given in arbitrary units which may be converted into feet-per-minute values by means of the calibration curve shown in Fig. 5.

The third variable, temperature, affects ink tack and is held constant within narrow limits, as described above. The effect of ink temperature on pick point is shown in Table I. The data show a half-unit increase in print speed passed per 1.0°C. In the test procedure described, the plate cylinder temperature is main-

**Table I. Effect of Ink Temperature on Print Test Passed**[a]

| *Ink temperature,*[b] *°C.* | *Print test passed* |
|---|---|
| 23.8 | 7–7.5 |
| 24.3 | 7.5 |
| 24.8 | 7.5–8 |

[a] Test sample was a mill-coated paper containing a protein binder. Ink used was IPI No. 3 pick test black.
[b] Temperature of plate cylinder at a point close to printing surface.

**Table II. Effect of Weight of Ink Used on Print Test Passed**

| Weight of ink used: Total mg. applied | Mg./sq. in. of plate surface[a] | Depth of ink film, mils[a] | Print test passed[b]: Paper no. 1 | Paper no. 2 | Appearance of printed films[c] |
|---|---|---|---|---|---|
| 28 | 2.6 | 0.15 | 9+ | 4.5 | Light |
| 33 | 3.0 | 0.18 | 8.5 | 4+ | |
| 38 | 3.5 | 0.20 | 8− | 4 | Medium |
| 43 | 3.9 | 0.23 | 7.5+ | .. | |
| 48 | 4.4 | 0.26 | 7.5 | 4 | Heavy |
| 53 | 4.8 | 0.28 | 7.5 | 4 | |
| 66 | 6.0 | 0.35 | 7.5+ | 4+ | |

[a] Calculated values based on weight of ink applied to inking roller and plate cylinder (combined surface area of 11.0 sq. in.) assuming equal film thickness on the two surfaces.
[b] The end point is usually read to the nearest half unit. Plus and minus signs are used to indicate on which side of the nearest half unit the end point appeared to be.
[c] These are rough visual ratings obtained by comparison with samples of commercial printing.

tained within ±0.2°C., which is considered adequate control. Under constant test conditions the normal variation in the pick point of strips cut from the same sheet is ±0.25 unit. Factors which introduce no greater variation in pick point than ±0.25 unit are considered to be under satisfactory control.

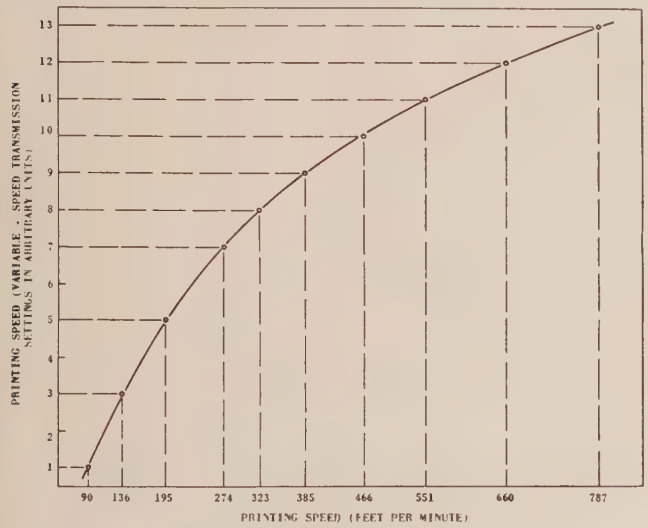
PRINTING SPEED (VARIABLE - SPEED TRANSMISSION SETTINGS IN ARBITRARY UNITS)
PRINTING SPEED (FEET PER MINUTE)
90 136 195 274 323 385 466 551 660 787

*Fig. 5. Variable-speed transmission calibration*

In the adjustment of ink quantity and impression pressure our objective has been the attainment of a good quality print. However, certain modifications to this approach have been introduced for the purpose of improving the flexibility and dependability of the test method.

The amount of ink used is about twice the amount required to produce a good quality print on a high smoothness coating at a low printing speed. Use of a large amount gives a substantial working range in ink weight over which the pick point is essentially constant (Table II).

**Table III. Effect of Printing Speed and Weight of Ink Used on Transfer of Ink to Paper[a]**

| Weight of ink used: Total mg. applied[b] | Mg./sq. in. of plate surface[c] | Depth of ink film, mils[c] | Ink transferred to paper, mg./sq. in. of solid print[b]: Printing speed: 2 | 7 | Weight % of ink transferred: Printing speed: 2 | 7 |
|---|---|---|---|---|---|---|
| 28 | 2.55 | 0.15 | 1.19 | 1.16 | 47 | 45 |
| 38 | 3.46 | 0.20 | 1.60 | 1.42 | 46 | 41 |
| 48 | 4.36 | 0.26 | 2.02 | 1.68 | 46 | 39 |

[a] Test sample was a mill-coated paper. Ink used was IPI No. 3 pick test black.
[b] Observed values.
[c] Calculated values.

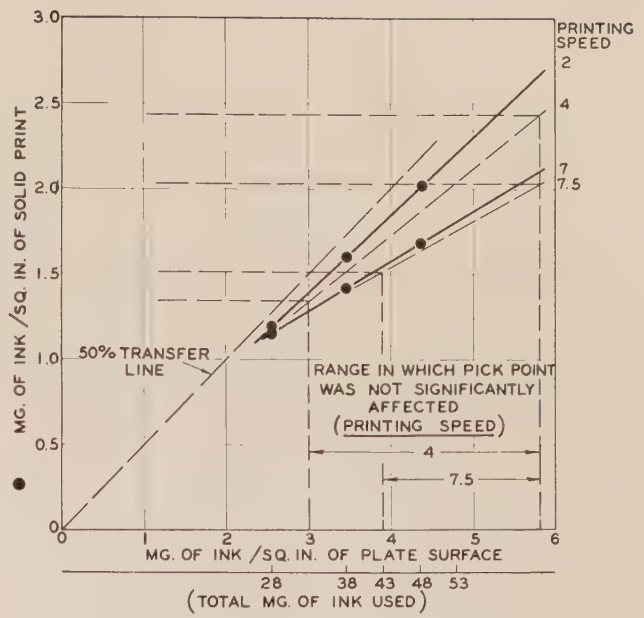


*Fig. 6. Weight of ink applied to plate vs. weight of ink printed*

Assuming a constant percentage of ink transfer from plate to paper it follows that there also is a substantial range in weight of printed films over which no significant change in pick point occurs. At medium printing speeds, actual percentage of ink transferred was found to diminish moderately as weight of ink applied to the plate was increased (Table III). Acceptable reproducibility in weighing printed films was achieved by working rapidly in a constant-humidity room and avoiding direct handling by using rubber finger cots.

Despite the change in percentage transfer, there was a wide range in weight of ink printed over which the pick point was substantially constant (Fig. 6). Thus it seems that some variations in the factors which affect ink transfer can be tolerated in the heavy ink range with no apparent effect on test results. Some of the factors believed to affect ink transfer are: (1) speed of printing (Fig. 6), (2) ink receptivity of the coating, and (3) coating smoothness. Examples of variations in ink transfer with coated papers from different sources are given in Table IV.

Impression pressure is controlled by varying the amount of packing with which the test strip is underlaid. Regular 6-point manila packing is used for this purpose, the thickness being near the minimum necessary to produce a good-quality print. In fact, there is

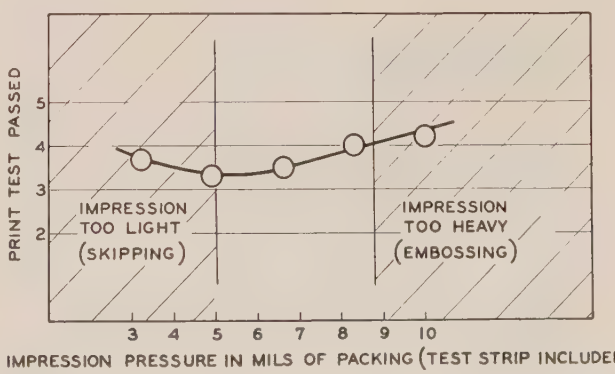
PRINT TEST PASSED
IMPRESSION TOO LIGHT (SKIPPING)
IMPRESSION TOO HEAVY (EMBOSSING)
IMPRESSION PRESSURE IN MILS OF PACKING (TEST STRIP INCLUDED)

*Fig. 7. Impression pressure vs. pick point and quality of print*

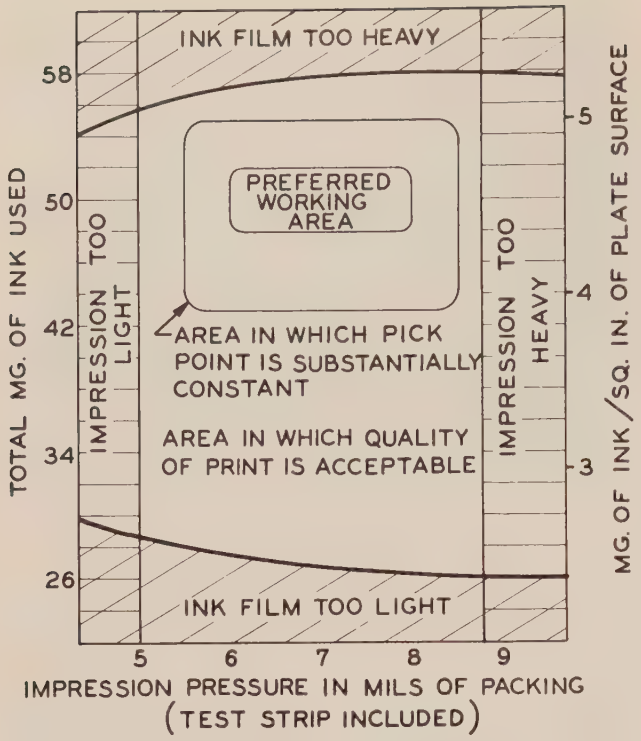


*Fig. 8. Effect of ink weight and impression pressure on quality of print and pick point*

a substantial range in impression pressure over which no significant change in pick point occurs (Fig. 7). Impression pressure is the amount (in mils) by which the combined thickness of the packing and test strip exceeds the clearance between the plate and the impression cylinder.

The practical working range in impression pressure is 5.5 to 8.5 mils, preferably 6 to 8 mils. The amount of impression mark obtained in the 6 to 8-mil range compares favorably with that obtained in good quality letterpress printing.

The area of good quality printing in terms of impression pressure and weight of ink used is shown in Fig. 8. The preferred working area for the purpose of pick testing is defined by the small rectangle. Maximum flexibility and dependability of the test method are achieved by using a set of conditions within this rectangle. In the preferred area ink clean-up after printing is not necessary unless appreciable coating material has adhered to the plate cylinder. Suitable ink replacement is obtained by determining, within ±20%, the

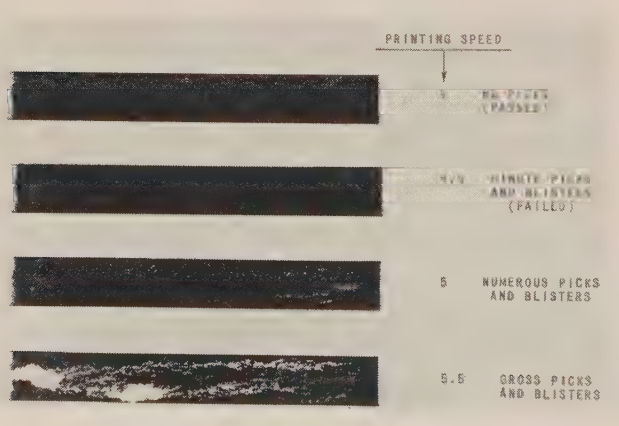


*Fig. 9. Test strips showing effect of increasing speed of printing*

**Table IV. Effect of Changes in Nature of the Sample Under Test on Ink Transfer**

| *Sample no.*[a] | *Ink on plate,*[b] *mg./sq. in.* | *Ink printed,*[c] *mg./sq. in.* | *Weight % of ink transferred* |
|---|---|---|---|
| 1 | 3.14 | 1.47 | 47 |
| 2 | 3.14 | 1.37 | 43 |
| 3 | 3.14 | 1.43 | 46 |
| 4 | 3.14 | 1.64 | 52 |
| 5 | 3.14 | 1.43 | 46 |
| 6 | 3.14 | 1.54 | 49 |

[a] Sample nos. 1 and 2 were coated in the laboratory; all others were mill-coated papers.
[b] Calculated values. Weight of IPI No. 3 pick test black ink applied to ink roller and plate cylinder was 36 mg.; total roller surface area was 11.5 sq. in.
[c] Observed values.

weight of ink printed onto the test strip and using a shim to set the ink syringe to deliver the proper amount.

Base stock direction is a factor which affects pick point. Strips cut in the machine direction usually pass a printing speed 1 to 3 units higher than strips cut in

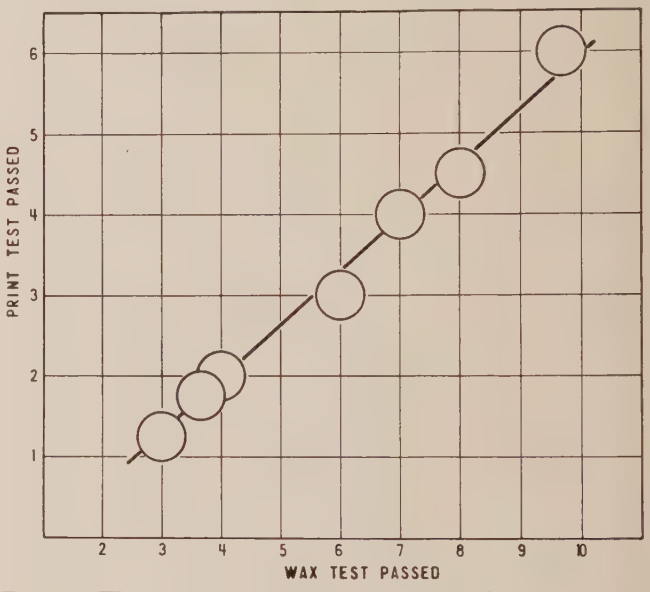


*Fig. 10. Wax test vs. print test on a series of casein-bound coatings*

the cross-machine direction. This is not surprising in view of what is known of the two-directional nature of a paper web. We have arbitrarily chosen to cut all test samples in the machine direction. In the case of low-strength coatings, stock direction may be of less importance.

Following adjustment of the operating variables as described above, the end point is determined by in-

**Table V. Summary of Statistical Analysis of Dennison Wax Test and Hercules Print Test Values vs. Commercial Printing Press Pick-Resistance Ratings**

| *Correlation coefficient* (r) | *Degrees of freedom* | *Equation of regression line*[a] | *95% Confidence limits* ($y \pm t\sigma_r$) |
|---|---|---|---|
| Dennison wax test vs. press pick-resistance rating (nonthermoplastic adhesives only): | | | |
| 0.976 | 6 | $y = 2.14x - 6.1$ | ±2.6 |
| Dennison wax test vs. press pick-resistance rating (including all nonthermoplastic and thermoplastic adhesive materials): | | | |
| 0.562 | 10 | Not calculated | |
| Hercules print test vs. press pick-resistance rating (including all nonthermoplastic and thermoplastic adhesive materials): | | | |
| 0.963 | 10 | $y = 1.6x - 1.4$ | ±2.8 |

[a] Where $x$ is the maximum Dennison wax test (first equation) or Hercules print test (second equation) passed and $y$ is the commercial press pick-resistance rating. These equations are applicable only under the paper coating and printing conditions employed in these trials.

creasing the speed at which successive strips are printed until coating failure occurs (see Fig. 9). The number of sheets which must be tested to obtain a reliable average test value is largely determined by the uniformity of the coated paper under test.

The final proof of a bonding strength or pick resistance test is the establishment of a correlation between test results and actual pressroom performance. There are substantial problems attendant to the development of such a correlation; however, a good part of the proving-in process can be carried out in the laboratory. For example, we know that, in general, bonding strength or pick resistance should increase with per cent binder based on the pigment.

Normal relationships between pick point and binder content have been consistently obtained in the laboratory. On casein-bound coatings good correlation has been obtained between print test and Dennison wax test values as binder content, raw stock and calendering treatment were varied (Fig. 10). This is to be expected because the Dennison wax test normally gives dependable results on casein-bound coatings.

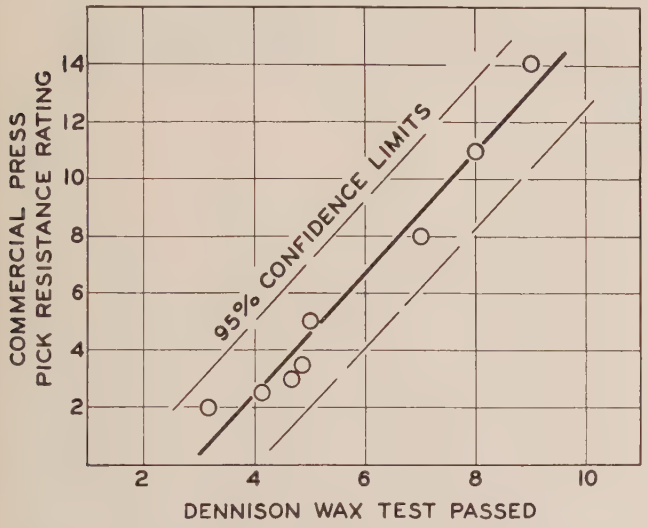


*Fig. 11. Dennison wax test passed vs. pick-resistance rating on a commercial press: coated papers containing nonthermoplastic binders only*

In an effort to establish further the reliability of the Hercules print tester, a group of experimental mill-coated papers was made using various concentrations of nonthermoplastic binders alone and in combination with thermoplastic binders. These papers were tested by the Dennsion wax test and the Hercules print tester, then submitted to printing trials on a Miehle Vertical Model V50 printing press using a special proof plate. The variables considered in the printing trials were: (1) press speed (3100 to 4500 impressions per hour) and (2) ink tack. The inks used were halftone, bond, and heavy bond inks, alone and in various combinations to produce a tack series. Body gum was used in some combinations in order to extend the tack series.

The papers were given relative pick-resistance ratings based on their performance at various combinations of ink tack and press speeds used in the printing trials. A statistical analysis of the large volume of data obtained showed the following:

1. A significant correlation (Fig. 11) was found between Dennison wax test values and press pick-resistance ratings for the papers containing nonthermoplastic adhesives.

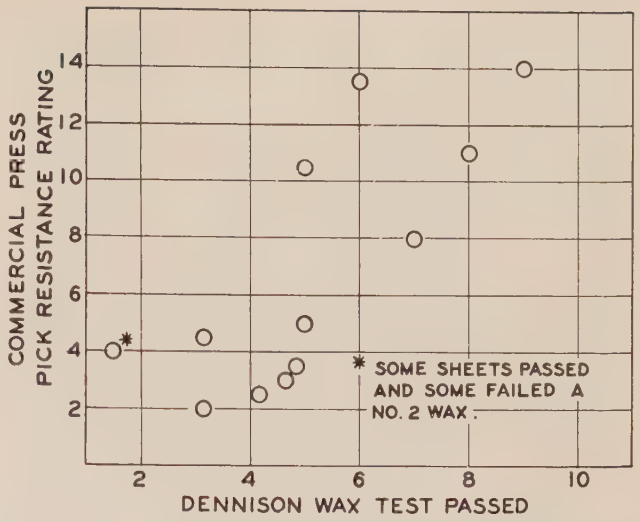


*Fig. 12. Dennison wax test passed vs. pick-resistance rating on a commercial press: coated papers containing both thermoplastic and nonthermoplastic binders*

2. No significant correlation (Fig. 12) was found between Dennison wax test values and press pick-resistance ratings when the papers containing some thermoplastic adhesive material were included with those containing no thermoplastic material.
3. A significant correlation (Fig. 13) was found between the Hercules print tester values and press pick-resistance ratings regardless of the type (nonthermoplastic or thermoplastic) of adhesive materials used.

A summary of pertinent statistical data is given in Table V.

In another study, print tester data were collected on a group of 27 samples of commercially coated paper of known pressroom performance including several papers which had failed. The samples varied widely in paper properties and in the conditions under which they were printed. However, there were pairs of samples of common origin printed under identical conditions in which one showed picking and the other did not. In all such cases, the print tester data showed the picked sample to be weaker than the unpicked companion sample.

There are two purposes which this test method can serve: (1) it can be used in experimental studies of coated paper components in which the components are varied singly, or (2) it can be used to measure the

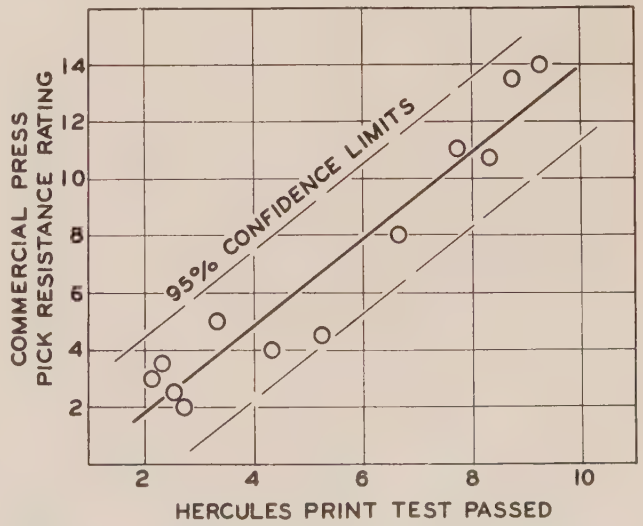


*Fig. 13. Hercules print test passed vs. pick-resistance rating on a commercial press: coated papers containing both thermoplastic and nonthermoplastic binders*

strength of a wide variety of coated papers as an aid to the paper converter and the printer. In the former application, we have found the Hercules print tester to be effective. The latter application requires the establishment of a correlation based on experience and a large number of tests. Two efforts to correlate print test data with press performance on a variety of coated papers have already been made with very encouraging results.

The print tester also offers considerable promise as a tool for measuring aspects of printability other than pick resistance. In fact, an operator cannot test a group of papers without consciously or unconsciously making observations on such properties as smoothness, affinity of the paper for ink, and rate of ink drying.

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Presented at the Second Coating Conference sponsored by the Technical Association of the Pulp and Paper Industry, Boston, Mass., April 18–20, 1951.


# The Mechanism of Gloss Development in Clay-Coated Sheets


LEROY A. WOODWARD and S. C. LYONS



**About 1932, W. T. Maloney discovered that when an ordinary papermaking kaolin was separated into two particle-size fractions—one being finer than 2 mu diameter, while the other was coarser than that diameter—the fine-particle clay produced paper coatings of surprisingly greater gloss and hiding power than the original clay. The above mentioned 2 mu dimension is also the size at which kaolin particles undergo a marked change in shape. Particles finer than 2 mu are predominantly flat pseudo-hexagonal plates, whereas the particles coarser than this are almost entirely cemented stacked aggregates of these fine single plates. When during the coating operation these small flat-plate particles are spread upon a paper web, they will tend to assume a preferred orientation and lay flat on the surface of the sheet, thereby producing a coating whose surface will specularly reflect light. Such coatings will develop high gloss—both before and after calendering. Conversely, the coarser, and non-platey vermicular shaped particles assume a more random orientation, with many crystal edges and corners projecting through the surface of the coating. Such a surface produces a diffuse reflection of the incident light—with resulting dull or matte appearance. The minus 2 mu platey particle are shown to be about 1/10 as thick as their nominal diameter in contrast to the coarser particles which are more nearly isometric. Thus, a coating which embodies only the fine clay particles will have nearly ten times as many pigment interfaces with which to develop surface reflectance, which is a principal source of hiding power.**


About 1932, W. T. Maloney (*1*) discovered that when he removed most of the particles coarser than about 2 mu diameter from an ordinary paper coating clay containing about 60% of particles finer than 2 mu, he obtained a product which yielded paper coatings of strikingly higher gloss and hiding power than those produced by the original clay. He didn't explain the reason for this unexpected increase in gloss and opacity and it is, in fact, fairly certain that the state of the art at that time was such that he could hardly have been expected to understand the reason therefor. His discovery was based upon experimental observations, and his nomination of the 2 mu dimension was made from purely empirical considerations.


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### OPTIMUM PARTICLE SIZE FOR OPACITY AND/OR GLOSS

The leading experts (*2*, *3*, *4*) in the field of optics of pigmented films have realized the manifold and variable (and as yet undetermined) nature of the factors operating in such films and have been reluctant to unequivocally state "laws" governing the effect of pigment particle size upon the optical properties of such films. Perhaps their general attitude may be expressed in the words of Newman: "It has for many years been thought that the particle-size characteristics of pigments have profound influence on the properties of paint, or at least there has been an uneasy feeling that a correlation ought to exist even though so far the hope of its scientific demonstration has in many ways receded the more it has been pursued" (*2*). Nevertheless, there does seem to have been a general agreement among these authorities that—assuming ideal behavior for pigment particles, vehicle, etc.—at a particle diameter of about one-half the wave length

of the incident light, averaging approximately 0.25 mu, maximum scattering will occur. It should be remembered that these considerations took into account only the change in optical properties of the particles as they varied in size, but not any possible effects due to change in shape. This maximum in the scattering power of the particles will, for the paint compounder, probably influence the opacity of the film more than the gloss since paint gloss is mostly from the smooth surface of the vehicle. For paper coating where the pigment must produce both hiding power and gloss, the effects of the maximum scattering would be more confused, but still might be expected to have some influence.

This represents about the background of the effects of particle size on the properties of pigments that was known when Maloney started his work to make a superior paper coating. His approach had to be, however, greatly influenced by the fact that he had to use a natural raw material that already had a vast range of particle sizes in it. Economically, he could not select a particle size, or particle-size range, unless the recovery would be sufficient to justify the expense of making such selection. Thus, the approach was made with the knowledge of the desirable properties in mind and the knowledge that the product would have to be sold in a competitive market.

When his finding came out to show that the desirable properties of gloss and hiding power could be obtained with a product with a size range predominantly extending from 2 mu down to colloidal sizes, it was apparent that the known teachings of particle-size effects could be considered only very generally as guides and that there were perhaps other effects of equal or greater importance.

Throughout the preparation of many thousands of carloads of coating clay, it has been repeatedly noted that a marked increase in gloss of coated sheets made therefrom was not obtained unless at least 80% of the clay particles were finer than about 2-mu diameter.

These observed deviations from the theoretical behavior which had been postulated for spherical particles, suggested the thought that some dimension (perhaps the width of the crystal edges) of the clay particles at the critical 2-mu diameter might correlate with the light wavelengths in some manner so as to promote a specular, rather than a diffuse, reflection of the light.

## PRIOR KNOWLEDGE OF THE SHAPE OF KAOLINITE PARTICLES

At this point, it may be well to make clear that all current commerical paper-coating clays are produced from raw clays which are substantially pure kaolinite materials. Kaolin is one of several different types of clay minerals, e.g., montmorillonite (bentonite), dickite, halloysite, etc. Incidentally, when any substantial amount of these other clay minerals occurs as an impurity in the kaolin, it almost always renders it unfit for use as a paper-coating pigment for reasons which are beyond the scope of this paper.

Perhaps, therefore, at this point it would be well to retrace the history of general thinking relative to the shape of kaolin particles. More than 100 years ago, clays were studied at low powers of magnification by means of the ordinary optical microscope (*5*). A variety of shapes ranging from thick, hexagonal crystals (*6*) to elongated "wormlike" vermicular particle shapes (*7*) were ascribed to kaolinite particles. Incidentally, some of the older references must be read with discretion, because other clay minerals, such as dickite, were occasionally described therein as being kaolinite.

About the middle of the 1930's, with the introduction of the electron microscope, a new and basic insight into the physical nature of fine (i.e., $< 2$ mu) kaolinite particles became available, because now—for the first time—it became possible to resolve them and definitely determine their shape. They were seen to be elongated, hexagonal plates, and in the late 1940's, with the work of Johnson (*8*) and of East (*9*), using the recently developed technique of metallic vapor shadowing, they were further shown to be predominantly plates whose thickness averaged about $^1/_{10}$ to $^1/_{12}$ of their circular, projected image diameters. Incidentally, this "diameter," which was obtained by using a planimeter to measure the area of the crystal images and then calculate them back to circles, is seen to correlate surprisingly closely with their equivalent spherical diameter, as predicted by the method of Stokes during their preparation.

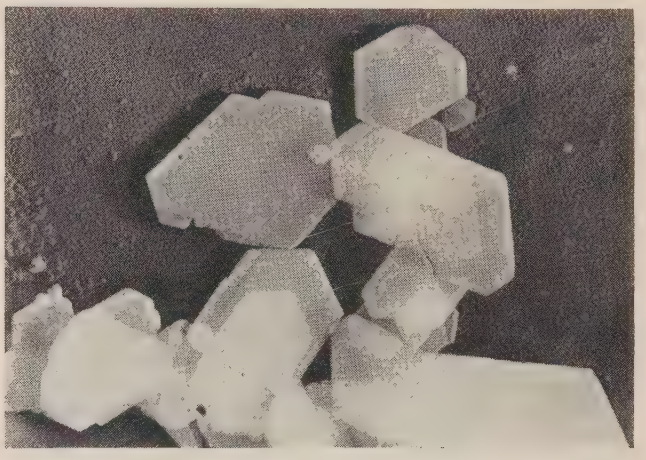

***Fig. 1. Kaolinite crystals—0.8 to 0.4 mu, W. H. East, prepared from Dry Branch, Ga., crude kaolin***

Note characteristic hexagonal plate structure

In Fig. 1 is shown a shadowed electron micrograph of Georgia kaolin particles of size between approximately 0.8 and 0.4 mu, this picture having been taken from Dr. East's thesis (*10*).

Studies made with the electron microscope were aimed at showing the small crystal form hitherto unrevealed by optical means. High magnification was therefore necessary with corresponding reduction in the field of view. In addition, specimen preparation methods were employed that tended to emphasize the small plates rather than the grosser particles. A large number of published electron micrographs of kaolinite showed only the platelike forms of the smaller particles and did not show any of the previously mentioned vermicules, or "worms." Thus, the thinking of the clay people changed from thinking in terms of the vermicules as the kaolinite particle form and considered only the platelike structure of the smaller particles.

## RECENT STUDIES OF PARTICLE SHAPE VS. PARTICLE SIZE

When, recently, it became necessary to determine definitely the correlationship between the particle size and/or shape of kaolin particles and their gloss-producing powers, a sample of Georgia kaolin was separated into a series of particle fractions of the following sizes—finer than 2 mu and monodisperse fractions of the following equivalent spherical diameters: 4, 7, 10, 15, and 20 mu. It was thought that micrographs of these might possibly reveal a series of crystal plates of increasing thickness and that the crystal edges of the particles larger than 2-mu diameter might be wide enough so that when spread upon a coated sheet they would cause an incident beam of light to be diffusely, rather than specularly, reflected. It should be noted here that the crude clay from which these fractions were prepared was subjected to the vigorous commercial treatments of dispersing, blunging, degritting, etc., and that the particles, when observed in the electron microscope, gave good agreement with the predicted Stokes' law diameters. This gives added weight to the feeling that the observed results were truly representative of the natural condition of the particles and were not the results of any artifact introduced during the preparation for observation.

These samples were sent to the State Engineering Experiment Station at the Georgia Institute of Technology in Atlanta for examination by means of the electron microscope.

As the electron micrographic study proceeded, it soon revealed a quite unexpected variation in the nature of the shape of kaolin particles in their different size ranges. The senior author obtained micrographs of a 7-mu clay particle in two different orientations which

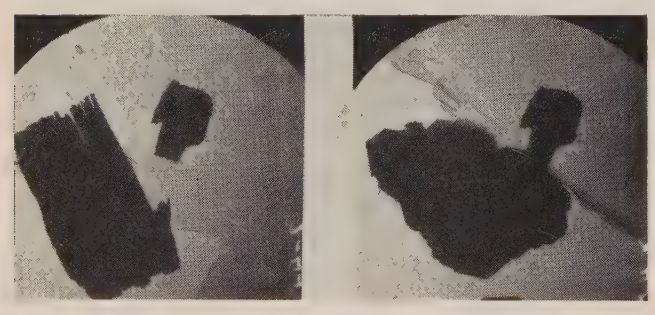

***Fig. 2. Kaolin particles—7 mu diameter***

Edgewise View: Note "laminated" end of particle, where the individual crystal plates are beginning to separate

Plane View: Note that upper end of particle shows characteristic hexagonal form. Note, also, that the largest indicated hexagon is approx. 2 mu diameter

were rotated nearly 90° from each other. These are shown above as Fig. 2.

These two micrographs were extremely enlightening. From them it became explicitly clear that the larger kaolin particles were no longer single crystal plates, but rather were cemented, stacked aggregates of the small, single-plate crystals. Sometimes, these could be considered as stacks of hexagonal "poker chips glued together." At other times, they partook of the nature of piled sheets of mosaic tiles which had been broken after the sheets had been cemented together. The nature of the kaolin vermicules, or "worms," became immediately apparent.

In Fig. 3 is shown an electron micrograph of the edges of a large kaolinite particle, wherein is clearly seen their laminate structure.

***Fig. 3. Large Georgia kaolinite particle (stack)***

Note projecting edges of component, individual, small crystal plates

In Fig. 4 are optical micrographs of 20-mu (micron) kaolinite particles wherein are seen typical kaolinite "stacks," or vermicules. Although the degree of resolution obtainable in this photograph is insufficient to reveal the details of the particle structure, it is, nevertheless, believed that the hazy lines parallel to the long, crystal axes are related in some way to rows of crystal plate corners. Also, several of the particles show clear evidence of laminated structure.

From the foregoing it should be clear that whereas the fine, i.e., below 2-mu diameter, kaolinite particles are predominantly single, flat crystal plates, those larger than 2 mu are stacked aggregates of these single, flat crystals. In order to determine the size at which the change from the flat, plate shape to the stacked form occurred, a very large number of micrographs—both by means of the optical and the electron microscope—were made. The 2-mu dimension appeared to be the point at which the transition took place. No single, flat crystal plate as large as 4 mu was found, although some as large as 2.6 mu were photographed. Conversely, thick stacked aggregates smaller than 2-mu diameter were seldom found.

The significance of this change of particle shape at 2 mu, with respect to its effect upon the gloss of clay-coated sheets, will be immediately apparent. Reference to Fig. 1 will show that the preferred orientation of the crystal plate particles is flatwise, parallel to the sheet. On the contrary, in Fig. 4 is seen that stacked aggregates have a less well-defined orientation, but in general they lie so that the crystal plates are perpendicular to the plane of the sheet surface. The individual plates, by virtue of their lying flat on the

surface of the sheet—like fish scales, will tend to reflect an incident beam of light specularly, in contrast to the relative diffuse reflection produced by the vermicular shaped particles.

In a correlation between the percentage of particles finer than 2 mu (plates) and the Ingersoll gloss readings made on sheets coated with a series of clays of progressively increased fine-particle content it is interesting to note that the gloss of the coatings increases gradually—and in linear fashion—with the per cent of clay particles under 2-mu diameter, up to a value of about 80% (as was originally taught by Maloney), but as the clay fineness increases above this value, the corresponding gloss readings rise at a much more rapid rate.

The calendering tends to reduce slightly the difference in gloss between the fine-particle clay coatings and those made from ordinary clays, but the contribution of the fine-particle plates to gloss is not significantly nullified.

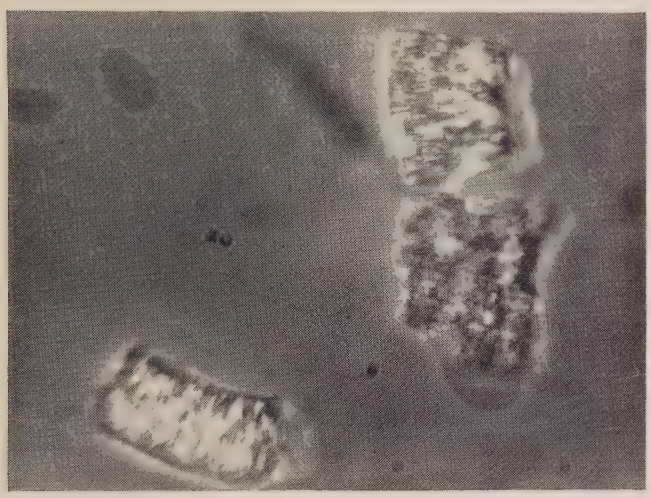

***Fig. 4. 20 mu kaolinite particles***

Note typical vermicular form and laminated structure

In this connection, it should be borne in mind that, when calendering to a predetermined value of gloss—rather than when the sheets are all calendered to an equal extent, the fine-particle clay superiority is most marked.

In Figs. 5 and 6 are shown, in a schematic cross section, coated sheets containing, respectively, fine-particle clays and ordinary coating clays which embody both plates and stacks. Incidentally, most fine-particle coating clays, as produced by the current, standard, commercial processing techniques, will contain very few—if any—particles coarser than about 6 mu.

The above-mentioned figures attempt to show that the fine-particle clays not only contain a vast predominance of plate-shaped crystals and are so small as to permit their easy orientation into a plane substantially parallel to that of the sheet, but also the few coarse particles, or stacks, they contain are small enough so that they permit these stacks to be fully embodied within the thickness of the coating film. By contrast, the ordinary coating clay, as shown in Fig. 6, will contain particles as coarse as 20 mu or so and are large enough so that they actually project through the surface of the coating film.

***Criticality of the 2-mu Dimension***

In order to establish just how critical the 2-mu dimension is, with respect to production of gloss, a

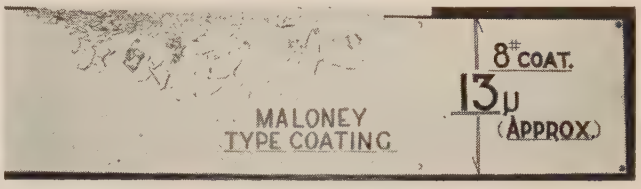


***Fig. 5. Fine-particle clay coating***

Schematic cross section

clay slip was separated into four fractions of different particle size, viz., finer than 2 mu, 2 to 5 mu, 5 to 10 mu, and 1 to 2 mu. Colors were then prepared from these clays and coatings prepared by means of the film applicator. Even a visual inspection of these coatings makes it perfectly clear that while there is very little, if any, increase in gloss between the 5 to 10-mu and the 2 to 5-mu fraction, a 2-mu and finer coating is much glossier than either of the others.

Incidentally, it can be seen that the increased gloss begins with the 2-mu particles rather than at some finer dimension, e.g., 1 mu, because the 1 to 2-mu fraction shows a markedly greater gloss than the 2 to 5-mu fraction.

Furthermore, the tabulation of hiding power index vs. particle size (Table I) shows that the platelike fractions (those finer than 2 mu) possess a substantially higher hiding power (opacity) per pound of coatweight than do the non-plate ("stacked") coarser particles.

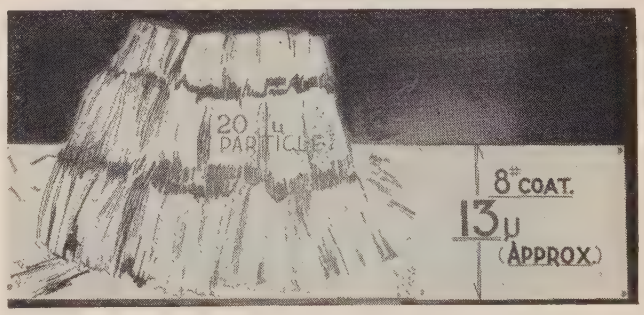


***Fig. 6. Ordinary coating clay***

Schematic cross section

There is a very logical explanation for this striking increase in hiding power of the platey (2 mu minus) particles as compared to the vermicular (2 mu plus) particles, since, as previously mentioned, the platey particles exhibit a thickness about $^1/_{10}$ as great as their diameter. There will be, in a coating of any specified thickness, about 10 times as many particles (for example, at 2-mu equivalent spherical diameter)—as-

suming that they lie parallel to the surface of the coating—as there would be if they were cubes or spheres or even vermicules.

**Table I**

| | Brightness | | | | |
|---|---|---|---|---|---|
| | *Raw stock* | *Coated* | *Increment* | *Coating weight* | *Increment/lb. coating* |
| 5–10 mu | 56.3 | 64.7 | 8.4 | 8.0 | 1.06 |
| 2–5 mu | 56.3 | 66.9 | 10.3 | 7.3 | 1.47 |
| 2 and finer | 56.3 | 69.8 | 13.5 | 7.4 | 1.83 |
| 1–2 mu | 56.3 | 69.2 | 12.9 | 7.8 | 1.68 |

Since hiding power in films of this sort stems substantially from multiple reflection from optical interfaces, it will be obvious that these platelike particles provide a great many more such interfaces per unit thickness of coating than would particles of corresponding diameter, but of more isometric particle shape.

## ENGLISH VS. AMERICAN COATING CLAYS

Since there may arise in the minds of some, who have used English coating clays, a question as to how they compare with American clays in the foregoing respects, it may be mentioned that similar—though less extensive—electron micrographic studies have been made upon particle fractions prepared from English (primary kaolin) paper-coating clays. In general, the same characteristic change in particle shape is found as in the case of the secondary kaolins from Georgia and, furthermore, the change takes place at about the same 2-mu dimension.

***Fig. 7. Kaolinite stack (15 mu) from English coating clay***

However, the stacked aggregates, which are found in the residual English kaolins, are more often of a type which would have been formed by the breaking of piled "sheets of mosaic tiles" after the sheets had been cemented together. Although stacks of the columnar type were found, they were much less prevalent than in the American clays. There seemed also to be a tendency for the component crystal plates in the primary clays to be somewhat smaller and to assume a more random, or less parallel, orientation within the stacks than in the case of the secondary clays.

In Fig. 7 is shown a 15-mu (equivalent spherical diameter) particle taken from an English coating clay.

It seems quite possible that certain of the observed differences in coating properties (such as adhesive demand, etc.) of the English clays, as compared to the American clays, may stem in part from these differences in the shape and surface structure of their respective stacks.

## CONCLUSIONS

From the foregoing micrographic studies it became clear that the kaolins, from which paper-coating clays are currently prepared, consist essentially of particles of two general different shapes. The fine particles are predominantly flat (frequently single), elongated, hexagonal plates, whereas the coarser particles are stacked aggregates of these smaller crystal plates. The single flat crystals are seldom found to be of diameter greater than that corresponding to about 2 mu (equivalent spherical diameter), whereas thick stacks are seldom found whose size is smaller than this. The fact that these fine (flat) kaolinite particles yield glossier coatings is rationalized by consideration of micrographs which show clearly the tendency of the fine particles to exhibit a preferred orientation parallel to the surface of the coating, whereas the coarser stacked particles prefer to deposit themselves in such position that the edges of their component crystal plates are normal to the coating surface.

Pulldowns prepared from clay fractions just finer than 2-mu diameter are strikingly glossier than those made from clays which are very slightly coarser than this value. The change in gloss is shown to increase markedly at about the 2-mu diameter.

The reason for the observed increase in hiding power, or opacity, of particles finer than the critical 2-mu dimension is seen to reside in the fact that the thin-plate crystals provide—in the limited available coating thickness—a great many more reflecting interfaces than would be the case if the particles were of more isometric shape.

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Received June 19, 1951. Presented at the Second Coating Conference sponsored by the Technical Association of the Pulp and Paper Industry, Boston, Mass., April 18–20, 1951.

The authors wish to express their appreciation for the assistance of the State Engineering Experiment Station at the Georgia Institute of Technology in Atlanta, Ga., in connection with the preparation of the micrographs presented herein; to the staff of the Georgia Kaolin Co. Laboratories at Dry Branch, Ga., for the preparation of monodisperse fractions, pulldowns, etc.; and to C. G. Albert and Louis Petty of the Edgar Co. Laboratory staff at McIntyre, Ga., for the preparation of coated sheets and gloss measurements thereon.

# Comparison of Fractional Solution and Fractional Precipitation as Applied to Cellulosic Materials

EMIL HEUSER and LEIF JÖRGENSEN

**The nitrates of cotton linters and various wood pulps were subjected to fractional solution and fractional precipitation. Step curves, drawn from the weights and the D.P.'s of the fractions, showed the difference in chain-length distribution, depending upon which of the two methods was chosen. Fractional precipitation would seem to be preferable since it is capable of accomplishing a more thorough subdivision of the cellulosic materials. This was demonstrated further by the refractionation of apparently uniform fractions of a Mitscherlich pulp. The reliability and the reproducibility of the method were demonstrated by the refractionation of blended fractions and by comparing actually obtained with calculated values.**

For some time, chain-length distribution studies in the Cellulose Laboratory at The Institute of Paper Chemistry were carried out with the aid of the fractional solution method. The results revealed a somewhat unexpected uniformity in the degree of polymerization (D.P.) in the upper ranges for all cellulosic materials investigated, regardless of their origin. These findings aroused some suspicion as to the value of the method for separating cellulose chain molecules above a certain average length to a reasonable extent and suggested a check on this suspicion by using other fractionation methods. Fractional precipitation appeared to be the most convenient choice. Its tentative application in a few cases led to a systematic comparison between the two methods, using a wide variety of cellulosic materials as regards source and average D.P. The following is a brief account of this study.

## CELLULOSIC MATERIALS USED

1. Cotton linters, bleached, from the Hercules Powder Co. Average D.P. 1660.
2. Mitscherlich pulp from spruce, unbleached. Average D.P. 1880.
3. Kraft pulp from western hemlock, unbleached. Average D.P. 1570.
4. Commercial dissolving pulp (I) for the manufacture of rayon pulp. Average D.P. 980.
5. Commercial dissolving pulp (II) for the manufacture of cellulose acetate. Average D.P. 920.
6. Laboratory high D.P. dissolving pulp. Average D.P. 1470.
7. Laboratory medium D.P. dissolving pulp. Average D.P. 545.

## METHODS USED

The cellulosic materials were converted into their nitrates, as described in a previous publication (*1*). The nitrates were weighed and the (specific) viscosities measured in acetone, employing an overflow-type Ostwald viscometer and allowing the concentration to remain at or below 0.1500% at 20° ± 0.02. The specific viscosities were converted into molecular weights by using the Staudinger function:

$$\text{D.P.} = \eta_{sp.}\, c = cK_m$$

and a $K_m$ value of $11 \times 10^{-4}$.* The concentration ($c$) was measured in grams per liter.

The nitrates were then subjected to both fractional solution and fractional precipitation procedures.

*The fractional solution method* was used in the Cellulose Laboratory of The Institute of Paper Chemistry during the war years and thereafter for chain-length distribution studies on many samples of various cellulosic materials.† Ethyl acetate (C.P.) was used as the solvent and 95% ethanol (U.S.P.) as the nonsolvent. The weighed and dried cellulose nitrate (0.5 to 1.0 gram) was transferred to pear-shaped centrifuge tubes of about 100 ml. capacity. The first of a series of solvent mixtures (see below) was poured into the tubes; these were securely stoppered and placed on an International shaking machine. After 40 to 60 minutes of shaking, separation of the solution from the undissolved portions of the nitrates was effected by centrifuging at 2000 r.p.m. The supernatant liquor was carefully poured into a large weighing glass. The same solvent mixture was then added to the undissolved portions of the nitrate and the separation procedure repeated. The solution was evaporated almost to dryness on the water bath. The weighing bottle was then placed in a vacuum oven at 60°C. for 2 hours and left in a vacuum desiccator at room temperature overnight.

The number of nonsolvent-solvent mixtures and the proportions of nonsolvent to solvent employed in the fractionation procedure may be varied, essentially depending upon the average D.P. of the material to be fractionated. Table I shows the different mixtures used. Type A was used for cellulosic materials having D.P's from about 600 to 900, type B for materials between 900 to 1200, and type C for materials of about 1200 and higher.

*Fractional precipitation* was carried out as described previously (*1*).

## EXPERIMENTAL RESULTS

The weights and average D.P.'s of the individual

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* The present study preceded the one referred to in (*1*), in which a redetermined $K_m$ value of $11.6 \times 10^{-4}$ was used.

† The method is based on the work of Joseph E. Atchison (*2*), and on subsequent improvements, made first by R. Kjellgren and later, in cooperation with the former, by Wm. H. Shockley.

Table I. Solvent-Nonsolvent Mixtures Used in Fractional Solution

| Type | Fraction | I | II | III | IV | V | VI | VII | VIII | IX |
|---|---|---|---|---|---|---|---|---|---|---|
| A | Ethanol, parts | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | .. |
| | Ethyl acetate, parts | 10 | 12 | 14 | 16 | 18 | 20 | 22 | 24 | .. |
| B | Ethanol, parts | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 0 |
| | Ethyl acetate, parts | 10 | 12 | 14 | 16 | 18 | 20 | 22 | 24 | 100 |
| C | Ethanol, parts | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 0 | .. |
| | Ethyl acetate, parts | 12 | 16 | 18 | 20 | 22 | 24 | 26 | 100 | .. |

fractions of the various cellulosic materials mentioned earlier are listed in Tables II to IX for both procedures. The results are summarized in Table X. In the first four columns of this table are listed: the seven cellulosic materials studied; their average D.P.'s; the lowest and the highest D.P.'s obtained by the two fractionation methods; and the differences between the highest and the lowest D.P.'s for the two methods. Column 5 shows the ratios between the D.P. differences from the previous column. In column 6, the differences between the highest and the lowest D.P.'s for the upper 50% of the materials are compared for the two methods.

It is seen from the data in Table X that, in all cases, the D.P. ranges are wider for the fractional precipitation than for the fractional solution method and, therefore, the ratios between the D.P. differences (column 5) are far from being unity. In fact, they vary from 1.47 to 3.02, the greater part of the values being close to 2.0. This is interpreted to mean that the fractions, as obtained by the fractional precipitation method, comprise about twice as large a D.P. range as those obtained by the fractional solution method. The difference between the results obtained by the two methods is thus not confined to the upper long-chain portion although as may be seen from the last column, it is particularly great for the upper 50% of the samples.

This is well reflected in the step curves (Figs. 1–7), i.e., curves which were obtained by plotting the percentage weights of the individual fractions (abscissas) against their D.P.'s (ordinates). Each step represents one of the fractions of the cellulosic material under investigation.

As mentioned earlier, in all cases the fractional solution curves would seem to justify the conclusion that a considerable portion—i.e., at least 50% and sometimes up to 80% or more—of the cellulose samples under investigation, comprising the long- and medium-chain portions, had a rather uniform chain-length distribution. In contrast, the fractional precipitation curves reflect a much greater subdivision of the same D.P. ranges. Thus, the same cellulosic materials, which would seem to be rather uniform as a result of fractional solution, are rather nonuniform when evaluated on the basis of fractional precipitation. Undoubtedly, the

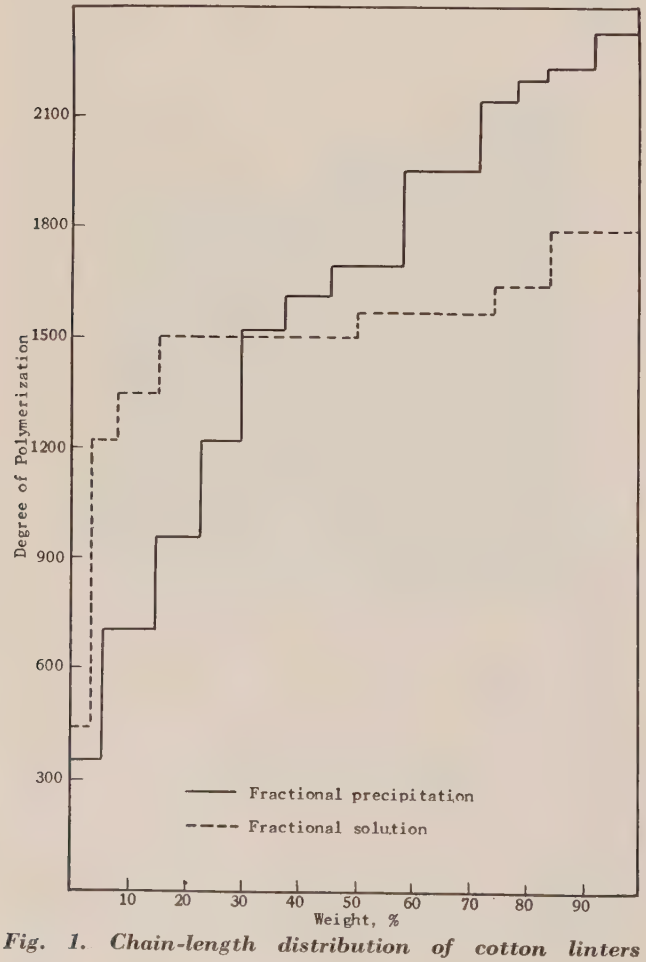


*Fig. 1. Chain-length distribution of cotton linters*

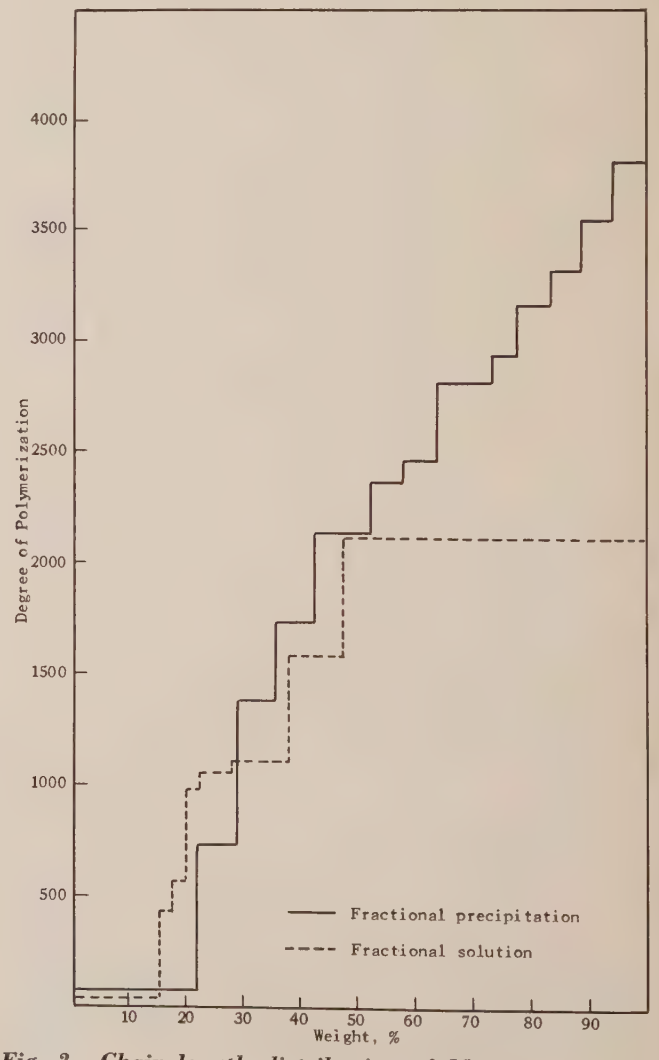


*Fig. 2. Chain-length distribution of Mitscherlich pulp*

**Table II. Fractionation of Cotton Linters**

Average D.P. 1660

| *Fraction* | *Weight, %* | *D.P. of fraction* |
|---|---|---|
| | 1. *Fractional Solution* | |
| 1 | 3.2 | 445 |
| 2 | 4.6 | 1225 |
| 3 | 7.4 | 1345 |
| 4 | 16.6 | 1505 |
| 5 | 19.0 | 1505 |
| 6 | 15.6 | 1795 |
| 7 | 9.8 | 1635 |
| 8 | 23.8 | 1575 |
| | 2. *Fractional Precipitation* | |
| 1 | 5.0 | 360 |
| 2 | 9.2 | 705 |
| 3 | 8.2 | 970 |
| 4 | 7.6 | 1215 |
| 5 | 7.4 | 1520 |
| 6 | 8.4 | 1620 |
| 7 | 13.0 | 1685 |
| 8 | 13.4 | 1950 |
| 9 | 6.6 | 2140 |
| 10 | 5.2 | 2200 |
| 11 | 8.8 | 2225 |
| 12 | 7.2 | 2335 |

latter technique is considerably more efficient than the former and, therefore, should be given preference in chain-length distribution work.

It will be noted that all cellulosic materials here investigated are rather polymolecular. This holds also for all the dissolving pulps. Although alkaline purification (which is used to produce dissolving pulps of this type) undoubtedly removes substantial amounts of the (alkali-soluble) short-chain material, it would seem that

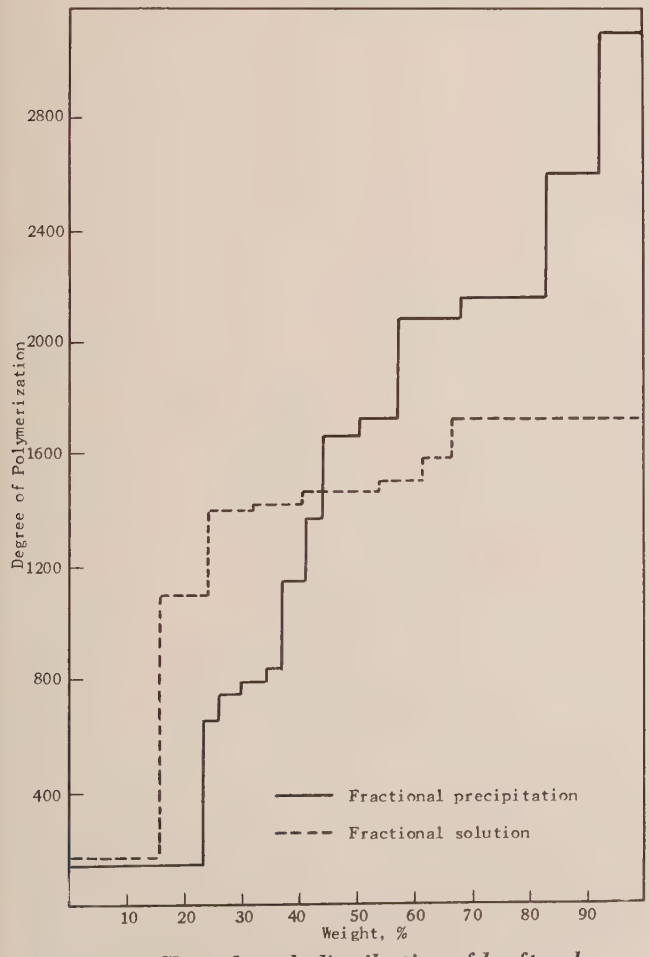


*Fig. 3. Chain-length distribution of kraft pulp*

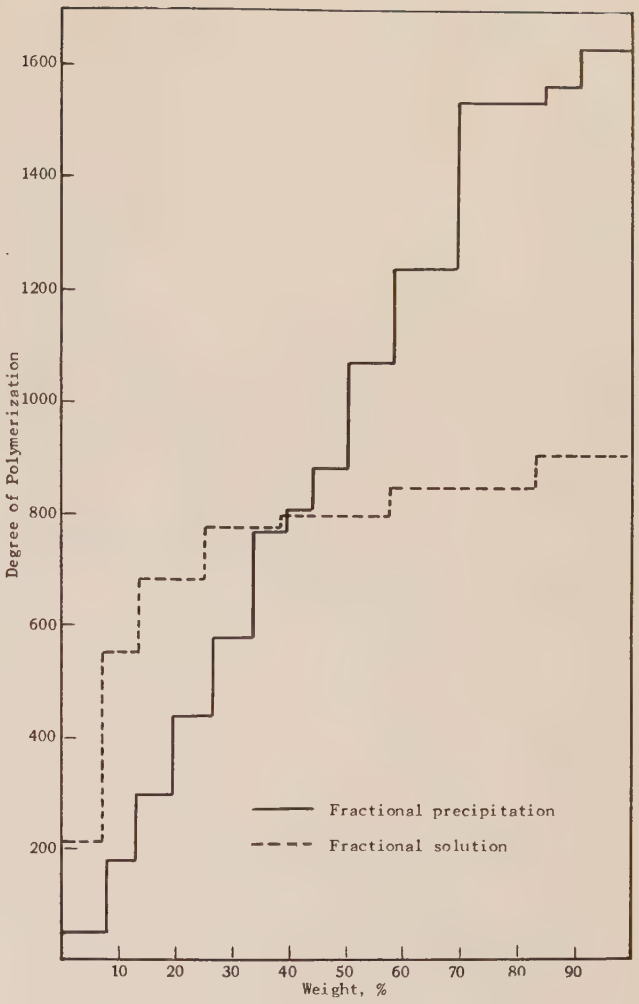


*Fig. 4. Chain-length distribution of commercial dissolving pulp I*

this process simultaneously attacks, by way of oxidation, the medium and longer chains and, thus, counteracts the homogenizing effect of alkaline extraction.

Table V and Fig. 6 show also the effect of "aging"—i.e., of heating the pulp in an oven at a temperature of

**Table III. Fractionation of Commercial Unbleached Mitscherlich Pulp**

Average D.P. 1880

| *Fraction* | *Weight, %* | *D.P. of fraction* |
|---|---|---|
| | 1. *Fractional Solution* | |
| 1 | 15.2 | 35 |
| 2 | 2.2 | 430 |
| 3 | 2.6 | 570 |
| 4 | 2.2 | 970 |
| 5 | 5.8 | 1040 |
| 6 | 10.2 | 1100 |
| 7 | 9.2 | 1580 |
| 8 | 52.6 | 2085 |
| | 2. *Fractional Precipitation* | |
| 1 | 22.0 | 105 |
| 2 | 7.2 | 725 |
| 3 | 6.0 | 1380 |
| 4 | 7.4 | 1725 |
| 5 | 9.6 | 2115 |
| 6 | 5.8 | 2360 |
| 7 | 5.6 | 2460 |
| 8 | 9.6 | 2815 |
| 9 | 4.4 | 2940 |
| 10 | 5.6 | 3170 |
| 11 | 5.8 | 3320 |
| 12 | 5.8 | 3520 |
| 13 | 5.2 | 3720 |

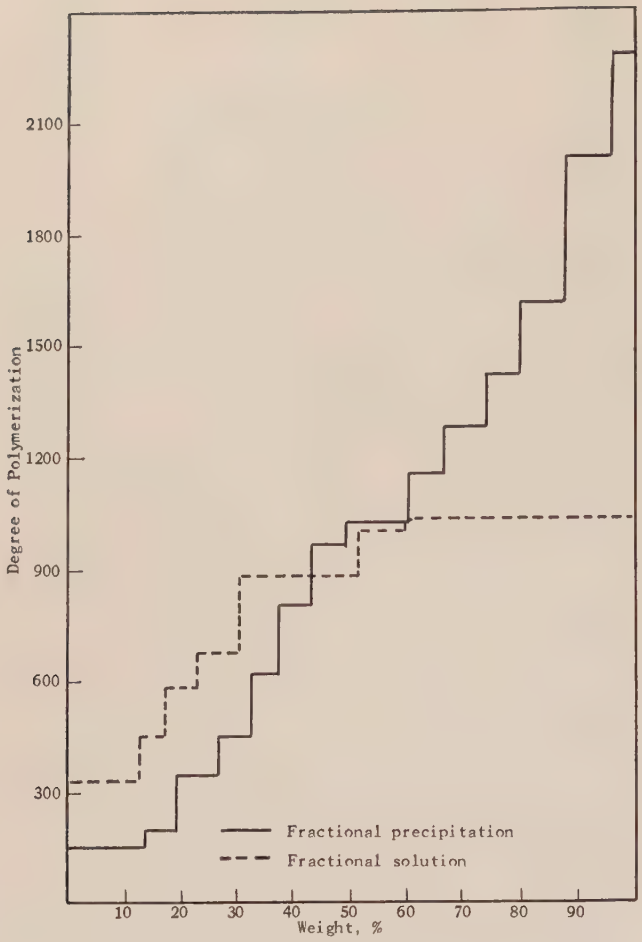


*Fig. 5. Chain-length distribution of commercial dissolving pulp II*

105°C. for 48 hours.‡ The homogenizing effect of this treatment upon the polymolecularity of the pulp is quite noticeable, and it is more distinctly shown by the fractional precipitation than the fractional solution

‡ Experiments by R. Kjellgren.

**Table IV. Fractionation of Laboratory Cooked Sulphite Pulp, Bleached and Alkaline-Refined**

Average D.P. 1470

| *Fraction* | *Weight, %* | *D.P. of fraction* |
|---|---|---|
| | 1. *Fractional Solution* | |
| 1 | 17.8 | 305 |
| 2 | 6.0 | 855 |
| 3 | 4.4 | 1010 |
| 4 | 7.0 | 1165 |
| 5 | 17.6 | 1280 |
| 6 | 8.0 | 1495 |
| 7 | 11.6 | 1535 |
| 8 | 17.4 | 1570 |
| 9 | 10.2 | 1505 |
| | 2. *Fractional Precipitation* | |
| 1 | 17.2 | 60 |
| 2 | 3.2 | 170 |
| 3 | 5.6 | 385 |
| 4 | 6.6 | 615 |
| 5 | 4.8 | 835 |
| 6 | 6.0 | 1160 |
| 7 | 6.0 | 1450 |
| 8 | 7.8 | 1725 |
| 9 | 15.0 | 2125 |
| 10 | 6.6 | 2470 |
| 11 | 9.4 | 2640 |
| 12 | 4.8 | 2780 |
| 13 | 7.0 | 3100 |

**Table V. Fractionation of Pulp Shown in Table IV After "Aging"**

Average D.P. 1115

| *Fraction* | *Weight, %* | *D.P. of fraction* |
|---|---|---|
| | 1. *Fractional Solution* | |
| 1 | 17.6 | 335 |
| 2 | 6.4 | 715 |
| 3 | 6.2 | 960 |
| 4 | 6.6 | 1045 |
| 5 | 13.8 | 1195 |
| 6 | 12.8 | 1345 |
| 7 | 36.6 | 1385 |
| | 2. *Fractional Precipitation* | |
| 1 | 13.6 | 60 |
| 2 | 6.2 | 165 |
| 3 | 9.4 | 415 |
| 4 | 11.8 | 565 |
| 5 | 9.2 | 935 |
| 6 | 5.4 | 1235 |
| 7 | 8.4 | 1450 |
| 8 | 2.8 | 1580 |
| 9 | 5.0 | 1745 |
| 10 | 11.2 | 1920 |
| 11 | 11.0 | 1960 |
| 12 | 6.0 | 2060 |

curves. As would have been expected, the effect of the aging is realized only at the expense of the average D.P., which is lowered from 1470 to 1115.

## REFRACTIONATION OF APPARENTLY UNIFORM PORTIONS OF MITSCHERLICH PULP BY FRACTIONAL PRECIPITATION

It was thought that the confidence in the fractional

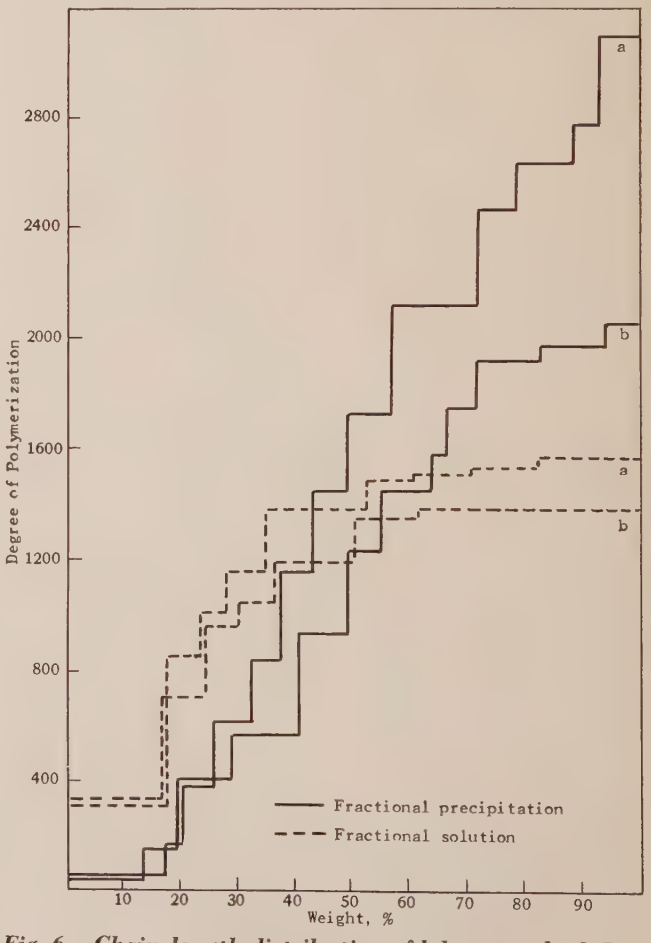


*Fig. 6. Chain-length distribution of laboratory high D.P. dissolving pulp*
a—Before aging; b—after aging.

**Table VI. Fractionation of Commercial Unbleached Kraft Pulp**

Average D.P. 1570

| *Fraction* | *Weight, %* | *D.P. of fraction* |
|---|---|---|
| | 1. *Fractional Solution* | |
| 1 | 15.6 | 175 |
| 2 | 8.4 | 1100 |
| 3 | 7.6 | 1400 |
| 4 | 9.0 | 1425 |
| 5 | 13.0 | 1465 |
| 6 | 7.6 | 1500 |
| 7 | 5.6 | 1595 |
| 8 | 33.2 | 1725 |
| | 2. *Fractional Precipitation* | |
| 1 | 23.4 | 165 |
| 2 | 2.4 | 645 |
| 3 | 4.2 | 755 |
| 4 | 4.0 | 785 |
| 5 | 2.4 | 835 |
| 6 | 4.6 | 1155 |
| 7 | 3.0 | 1365 |
| 8 | 6.6 | 1665 |
| 9 | 6.4 | 1725 |
| 10 | 11.0 | 2090 |
| 11 | 15.4 | 2180 |
| 12 | 8.8 | 2605 |
| 13 | 7.8 | 3105 |

precipitation method would be strengthened if it were possible to demonstrate that that portion of the pulp which appeared rather uniform according to the fractional solution method, could be shown actually to consist of a number of nonuniform fractions when refractionated by the fractional precipitation method.

Accordingly, the upper fractions which had been obtained from the pulp by fractional solution (Fig. 2, dotted line) and which comprised about 53% of the total with an average D.P. of about 2000, were redissolved in acetone and refractionated therefrom by fractional precipitation.

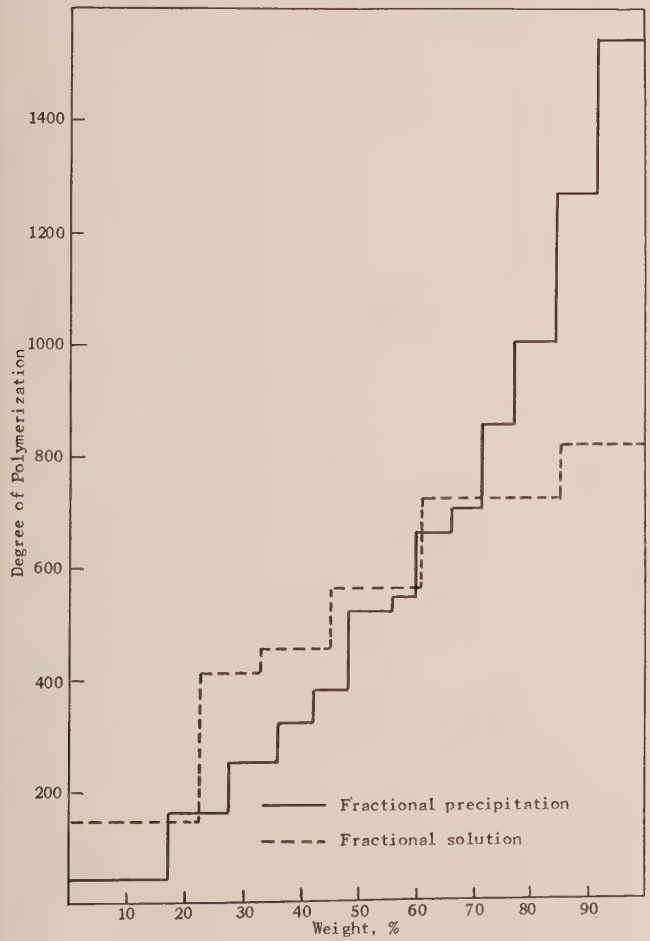


*Fig. 7. Chain-length distribution of laboratory medium D.P. dissolving pulp*

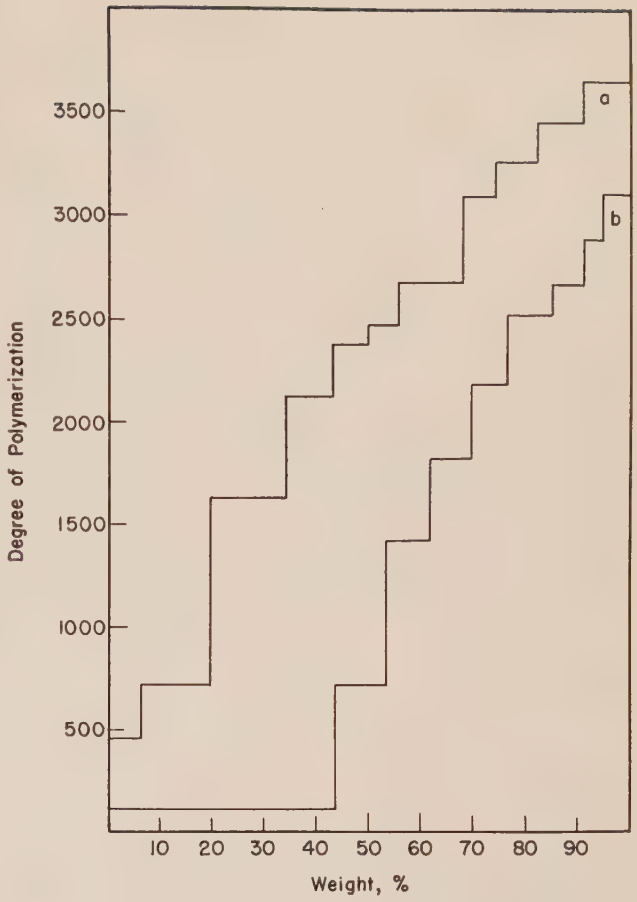


*Fig. 8. Chain-length distribution of Mitscherlich pulp; refractionated by fractional precipitation*

a—Upper portion; b—lower portion

Likewise, the lower portion of the pulp—i.e., the approximately 47% remaining, comprising D.P.'s between below 100 and about 2000—was refractionated by fractional precipitation because it would be expected that this portion could also be subdivided further.

**Table VII. Fractionation of Dissolving Pulp I**

Average D.P. 980

| *Fraction* | *Weight, %* | *D.P. of fraction* |
|---|---|---|
| | 1. *Fractional Solution* | |
| 1 | 7.4 | 210 |
| 2 | 6.0 | 555 |
| 3 | 11.2 | 685 |
| 4 | 13.6 | 775 |
| 5 | 19.6 | 800 |
| 6 | 25.4 | 855 |
| 7 | 16.8 | 905 |
| | 2. *Fractional Precipitation* | |
| 1 | 7.8 | 50 |
| 2 | 5.0 | 180 |
| 3 | 6.6 | 295 |
| 4 | 7.0 | 440 |
| 5 | 7.2 | 580 |
| 6 | 5.6 | 775 |
| 7 | 4.8 | 805 |
| 8 | 6.6 | 885 |
| 9 | 7.8 | 1075 |
| 10 | 12.2 | 1245 |
| 11 | 14.8 | 1535 |
| 12 | 6.2 | 1560 |
| 13 | 8.4 | 1635 |

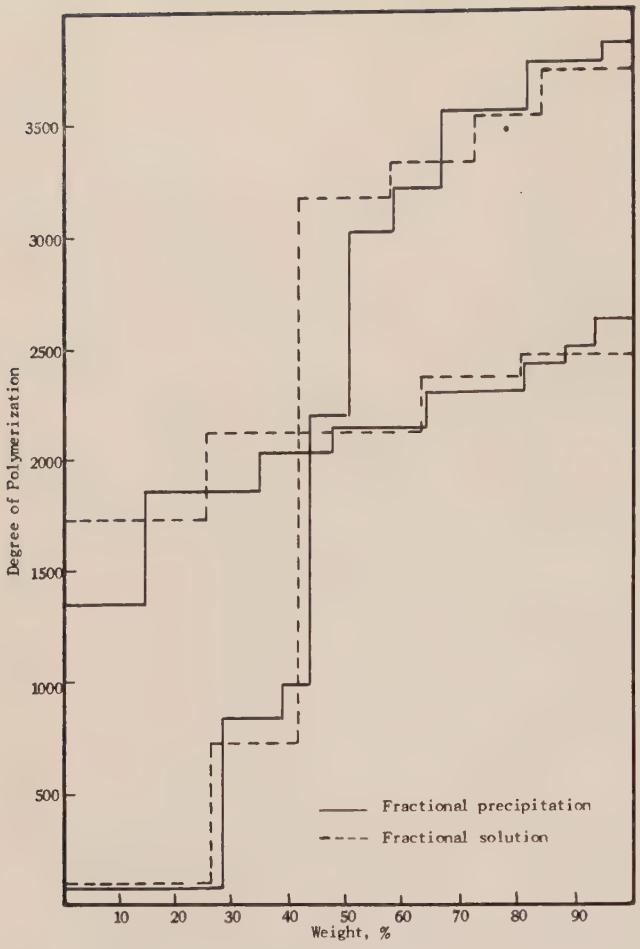


***Fig. 9. Chain-length distribution of Mitscherlich pulp; refractionation by fractional precipitation of blended portions***

Upper two curves: Blend of upper and lower fractions; lower two curves, blend of middle fractions

The results of these refractionation experiments, as shown in Table XI and Fig. 8, confirm these assumptions. It is seen that the upper portion of the pulp could be divided into a large number of fractions, ranging from a D.P. as low as about 450 to a value as high as about 3700.

**Table VIII. Fractionation of Dissolving Pulp II**

Average D.P. 920

| *Fraction* | *Weight, %* | *D.P. of fraction* |
|---|---|---|
| 1. *Fractional Solution* | | |
| 1 | 12.6 | 325 |
| 2 | 4.6 | 460 |
| 3 | 5.4 | 590 |
| 4 | 8.2 | 675 |
| 5 | 20.8 | 870 |
| 6 | 7.4 | 1000 |
| 7 | 41.0 | 1030 |
| 2. *Fractional Precipitation* | | |
| 1 | 13.8 | 135 |
| 2 | 5.2 | 215 |
| 3 | 7.6 | 345 |
| 4 | 5.6 | 455 |
| 5 | 5.0 | 625 |
| 6 | 6.0 | 800 |
| 7 | 6.0 | 970 |
| 8 | 11.0 | 1030 |
| 9 | 6.6 | 1140 |
| 10 | 7.2 | 1280 |
| 11 | 6.0 | 1425 |
| 12 | 8.0 | 1610 |
| 13 | 8.0 | 2005 |
| 14 | 4.0 | 2290 |

**Table IX. Fractionation of Laboratory Cooked Dissolving Pulp of Medium Average D.P. (545)**

| *Fraction* | *Weight, %* | *D.P. of fraction* |
|---|---|---|
| 1. *Fractional Solution* | | |
| 1 | 22.4 | 150 |
| 2 | 10.6 | 410 |
| 3 | 12.2 | 455 |
| 4 | 15.8 | 560 |
| 5 | 26.2 | 720 |
| 6 | 12.8 | 815 |
| 2. *Fractional Precipitation* | | |
| 1 | 17.0 | 45 |
| 2 | 10.4 | 160 |
| 3 | 8.2 | 250 |
| 4 | 6.4 | 320 |
| 5 | 6.4 | 380 |
| 6 | 7.2 | 520 |
| 7 | 5.2 | 540 |
| 8 | 5.8 | 660 |
| 9 | 4.8 | 705 |
| 10 | 6.0 | 855 |
| 11 | 7.4 | 1000 |
| 12 | 7.2 | 1275 |
| 13 | 8.0 | 1545 |

Likewise, the lower portion (Fig. 2, dotted line) was divided into a number of fractions ranging from a D.P. of about 100 up to a value of about 3100, the low-D.P. material having been increased to about 43%.

## REFRACTIONATION OF BLENDED FRACTIONS

In order to furnish further experimental evidence which would demonstrate the superiority of the fractional precipitation method and, at the same time, its reproducibility, certain upper and lower fractions of the

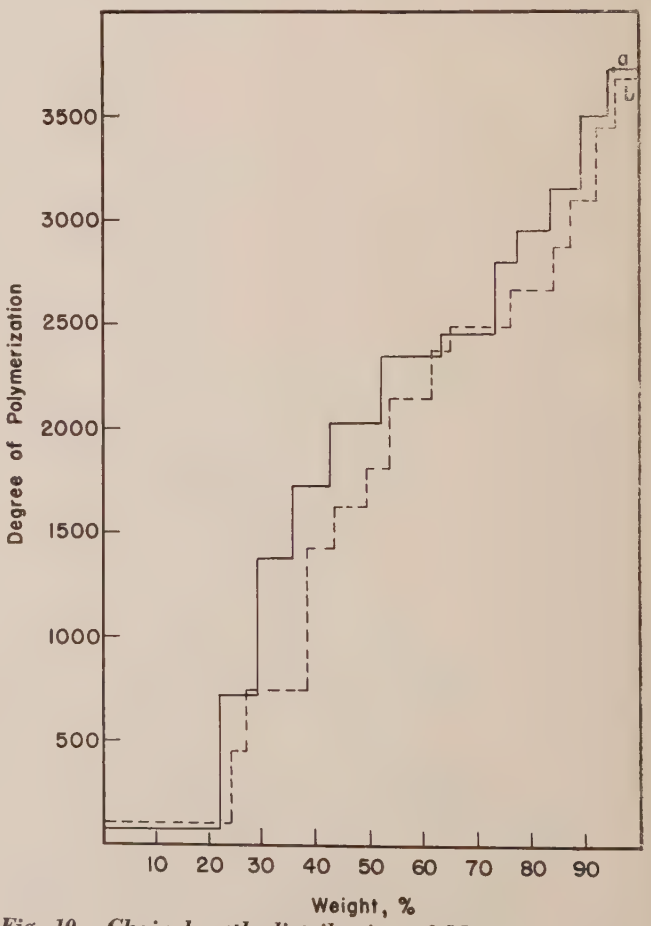


***Fig. 10. Chain-length distribution of Mitscherlich pulp***

a—Directly determined; b—calculated

**Table X. Comparison of D.P. Ranges Obtained by the Two Fractionation Methods**

| Cellulosic materials | Average D.P. | Lowest and Highest D.P. Solution Low | Solution High | Precipitation Low | Precipitation High | Difference between highest and lowest D.P. Solution | Difference between highest and lowest D.P. Precipitation | Ratio of D.P. difference solution/ precipitation | Difference between highest and lowest D.P. in upper 50% Solution | Difference between highest and lowest D.P. in upper 50% Precipitation |
|---|---|---|---|---|---|---|---|---|---|---|
| Cotton linters | 1660 | 480 | 1830 | 360 | 2335 | 1350 | 1975 | 1.47 | 290 | 650 |
| Commercial Mitscherlich pulp | 1880 | 110 | 2005 | 105 | 3720 | 1895 | 3615 | 1.91 | 0 | 1605 |
| Commercial kraft pulp | 1570 | 175 | 1725 | 165 | 3105 | 1545 | 2940 | 1.91 | 258 | 1650 |
| Commercial dissolving pulp I | 980 | 210 | 905 | 50 | 1635 | 695 | 1585 | 2.28 | 105 | 750 |
| Commercial dissolving pulp II | 920 | 313 | 1070 | 135 | 2425 | 760 | 2290 | 3.02 | 156 | 1350 |
| Laboratory high D.P. dissolving pulp | 1470 | 305 | 1570 | 60 | 3010 | 1265 | 3040 | 2.41 | 292 | 1650 |
| Laboratory high D.P. dissolving pulp after aging | 1150 | 335 | 1385 | 60 | 2060 | 1050 | 2000 | 1.90 | 190 | 975 |
| Laboratory medium D.P. dissolving pulp | 545 | 150 | 815 | 45 | 1575 | 665 | 1530 | 2.30 | 254 | 1025 |

**Table XI. Refractionation of Upper and Lower Fractional Solution Portions of Mitscherlich Pulp by Fractional Precipitation**

| Fraction | Weight, % | D.P. of fraction |
|---|---|---|
| | Upper Portion | |
| 1 | 6.6 | 460 |
| 2 | 12.8 | 735 |
| 3 | 14.8 | 1635 |
| 4 | 9.0 | 2130 |
| 5 | 7.0 | 2390 |
| 6 | 5.8 | 2480 |
| 7 | 12.4 | 2690 |
| 8 | 5.8 | 3100 |
| 9 | 8.6 | 3270 |
| 10 | 8.8 | 3460 |
| 11 | 8.4 | 3670 |
| | Lower Portion | |
| 1 | 43.2 | 105 |
| 2 | 10.2 | 760 |
| 3 | 8.6 | 1430 |
| 4 | 8.0 | 1825 |
| 5 | 6.8 | 2190 |
| 6 | 8.8 | 2520 |
| 7 | 5.6 | 2670 |
| 8 | 4.2 | 2895 |
| 9 | 4.6 | 3110 |

Mitscherlich pulp, as obtained by fractional precipitation, were blended by dissolving them in acetone and the blends refractionated by fractional precipitation.

**Table XII. Refractionation of Blends from Mitscherlich Pulp**

| Blend a Fraction | Blend a Weight, % | Blend a D.P. of fraction | Blend a—refractionated Fraction | Blend a—refractionated Weight, % | Blend a—refractionated D.P. of fraction |
|---|---|---|---|---|---|
| 1 | 26.6 | 105 | 1 | 28.8 | 80 |
| 2 | 14.9 | 725 | 2 | 9.8 | 855 |
| 10 | 15.8 | 3170 | 3 | 4.8 | 980 |
| 11 | 14.8 | 3320 | 4 | 6.8 | 2190 |
| 12 | 11.9 | 3520 | 5 | 7.8 | 3050 |
| 13 | 16.0 | 3720 | 6 | 8.8 | 3210 |
| | | | 7 | 14.8 | 3550 |
| | | | 8 | 12.8 | 3780 |
| | | | 9 | 5.6 | 3850 |
| **Blend b** | | | **Blend b—refractionated** | | |
| 4 | 25.6 | 1725 | 1 | 14.6 | 1350 |
| 5 | 38.2 | 2115 | 2 | 19.6 | 1850 |
| 6 | 16.6 | 2360 | 3 | 18.2 | 2025 |
| 7 | 19.4 | 2460 | 4 | 11.4 | 2130 |
| | | | 5 | 16.6 | 2290 |
| | | | 6 | 7.8 | 2410 |
| | | | 7 | 5.2 | 2490 |
| | | | 8 | 6.6 | 2610 |

**Table XIII. Distribution of Mitscherlich Pulp as Calculated from the Refractionation Data in Table XI**

| Fraction | Weight, % | D.P. of fraction |
|---|---|---|
| 1 | 22.9 | 105 |
| 2 | 3.1 | 460 |
| 3 | 11.4 | 750 |
| 4 | 4.5 | 1430 |
| 5 | 7.0 | 1635 |
| 6 | 4.2 | 1825 |
| 7 | 7.8 | 2160 |
| 8 | 3.3 | 2390 |
| 9 | 7.4 | 2500 |
| 10 | 8.8 | 2680 |
| 11 | 2.3 | 2895 |
| 12 | 5.2 | 3110 |
| 13 | 4.0 | 3270 |
| 14 | 4.1 | 3460 |
| 15 | 4.0 | 3670 |

The portions which were blended comprised four fractions of the upper portion, ranging in D.P. from 3170 to 3720, and two fractions of the lower portion, having D.P.'s of 105 and 725 (see part 2 in Table III). Likewise, the middle portion of the Mitscherlich pulp, comprising four fractions, ranging from a D.P. of 1725 to a D.P. of 2460 (see part 2 in Table III), were refractionated by fractional precipitation.

The results of the refractionation of the two blends are shown in Table XII (with the composition of the two blends on the left-hand side) and in Fig. 9. In this figure, the upper full-drawn curve represents the distribution obtained by refractionation of blend a and the lower full-drawn curve that of blend b. It is seen that there is a fairly good agreement between these two actually determined distribution curves and the dotted curves which were constructed from the data in the left-hand portion of Table XII.

Final proof of the suitability and reproducibility of the fractional precipitation method was obtained by comparing the actually determined (fractional precipitation) distribution of the Mitscherlich pulp (full-drawn curve in Fig. 2) with a curve which was calculated from the upper and lower portions (curves a and b in Fig 8). As will be recalled, these two portions originated from the fractional solution procedure. The result is shown in Table XIII and Fig. 10 (curve a representing the full-drawn curve from Fig. 2 and curve b representing the calculated curve). Again, the two curves are in fairly good agreement.

There would thus seem to be sufficient evidence for giving preference to the fractional precipitation technique. The essential reason why fractional solution is less efficient than fractional precipitation possibly lies in the fact that the initially fibrous and, therefore, quite accessible nitrate loses this structure as the extraction proceeds and becomes more and more of a gel, which interferes with a thorough extraction of chains.§ Obviously, this difficulty is not encountered with fractional precipitation.

§ This hypothesis is discussed in more detail in Leif Jörgensen's Doctoral Dissertation (*3*). As for gel formation, see also (*4*).


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Received Aug. 3, 1951.


# Determination of the Staudinger Constant for Some Cellulose Nitrates


EMIL HEUSER and LEIF JÖRGENSEN


The $K_m$ constant in the Staudinger equation, which expresses the relation between viscosity and molecular weight [degree of polymerization (D.P.)] thus:

$$\eta_{sp}/c = K_m \times M \qquad (1)$$

(wherein $\eta_{sp}$ is the specific viscosity, $c$ the concentration, and $M$ the molecular weight), and which is needed when the D.P. of cellulose derivatives is to be determined by the viscosity method, does not always have the same value. It varies not only with the pretreatment of the cellulose prior to its conversion into a derivative but also with the degree of substitution of the latter. Recently, some more exact data on these influences have become available. Thus, Schulz and Husemann (*1*) subjected one portion of a cotton sample to a hydrolytic treatment with aqueous 0.5 $M$ $KHSO_4$ solution at 60°C. and another to oxidation with oxygen in cuprammonium hydroxide solution, in both cases for increasing lengths of time. The average $K_m$ constant of the nitrates into which the two polyhomologous series were converted was $8.2 \times 10^{-4}$ for the hydrolysis series, and $10.2 \times 10^{-4}$ for the oxidation series. The nitrogen contents of the cotton nitrates were between 13.1 and 13.2%.

To what extent the nitrogen content influences the $K_m$ value may be seen from Table I, which contains data taken from a publication by Blaker, Badger, and Noyes (*2*).

On the basis of these two effects, it would be expected that the $K_m$ constant would likewise vary with the source of the cellulosic materials. In other words, it may be assumed that, because of the difference in the methods of isolation, a cotton nitrate would have a $K_m$ constant different from that of a wood pulp nitrate. On the other hand, one could expect to reduce, or even eliminate, the effect of the degree of substitution by introducing the same nitrogen content into the two types of cellulose.

It is readily seen [see also (*3*)] that these considerations make it necessary that the $K_m$ constant actually be determined experimentally if the viscosity method is to be used in connection with studies on the molecular weight of cellulosic materials, instead of relying upon those values which were "established" for the various cellulose derivatives by Staudinger and co-workers some time ago. This is necessary because these so-called "established" values hold, in reality, only for the particular types of cellulosic materials which were used in those earlier investigations.

In order to find the value for $K_m$ in the Staudinger function and thus to make use of as simple and fast a method as the viscosity method, the molecular weight of the cellulose sample has to be determined by one of the direct but more cumbersome methods. From the value thus obtained and the viscosity, the $K_m$ constant may be calculated thus:

$$K_m = (\eta_{sp}/cM) \qquad (2)$$

Today, for reasons of reliability and availability of equipment, $M$ is most frequently determined by the osmometric method, although its reliability is confined to the low and medium molecular weight ranges—i.e., between about 25,000 and 250,000 (corresponding to D.P.'s between about 150 and 1550). Below the lower limit, the molecules tend to diffuse out of the osmotic cell through the membrane and, above the upper limit, the osmotic pressure becomes too small to be measured with the desired accuracy. It may be added that the reliability in the upper limits has recently been somewhat extended by the introduction of the "osmotic balance" of Svedberg and Jullander (*4*, *5*). However, this improvement requires more complex equipment. Incidentally, the limitation of the reliability to medium and low molecular weights also holds more or less for the other direct methods (e.g., diffusion and sedimentation measurements in the ultracentrifuge and the light-scattering method) which are used, though less frequently, for checking the $K_m$ constant.

**Table I. Effect of the Nitrogen Content upon the $K_m$ Constant for Cotton Nitrate**

| Nitrogen, % | 11 | 12 | 13 | 13.5 |
|---|---|---|---|---|
| $K_m \times 10^{-4}$ | 6.0 | 6.7 | 8.2 | 10.0 |


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**Table II. Intrinsic Viscosity and Osmotic Pressure of Cotton Cellulose Nitrates in Acetone**

| *Intrinsic viscosity* | *Osmotic measurements* | | |
|---|---|---|---|
| | c, *g./l.* | p, *mm.* (*acetone*) | p/c |
| 1.210 | 3.14 | 6.3 | 2.00 |
| | 2.13 | 3.6 | 1.70 |
| | 1.57 | 2.3 | 1.44 |
| | 0 | .. | 0.86 |
| 0.912 | 2.67 | 6.7 | 2.52 |
| | 2.15 | 4.8 | 2.22 |
| | 1.91 | 4.0 | 2.09 |
| | 1.32 | 2.5 | 1.90 |
| | 0 | .. | 1.19 |
| 0.664 | 2.17 | 6.1 | 2.82 |
| | 1.53 | 3.8 | 2.51 |
| | 1.08 | 2.5 | 2.26 |
| | 0 | .. | 1.65 |
| 0.264 | 3.0 | 18.0 | 6.00 |
| | 1.90 | 10.2 | 5.37 |
| | 1.30 | 6.4 | 4.90 |
| | 0 | .. | 4.07 |
| 0.162 | 2.40 | 19.2 | 8.00 |
| | 1.60 | 12.2 | 7.60 |
| | 1.0 | 7.1 | 7.1 |
| | 0 | .. | 6.55 |

It has been pointed out frequently that an essential prerequisite for obtaining reliable molecular weight values of the high polymers is that the sample being investigated is as homogeneous as possible as far as its chain length is concerned. Therefore, all recent investigators have fractionated and refractionated their samples with the objective of eliminating as much as possible of both the very long- and the very short-chain material.

The study which is reported here is concerned with the determination of the $K_m$ constant of the nitrates of some of the cellulosic materials which were used in previous studies (*3*, *6*)—i.e., a cotton sample from an unopened boll, a commercial unbleached Mitscherlich pulp, and a commercial semichemical aspen pulp.*

These cellulosic materials were also used in a study in which an attempt was made to follow the course of their hydrolytic degradation, in both a heterogeneous and a homogeneous system, by ascertaining the changes which occurred in their average chain length and chain-length distribution.

The heterogeneous hydrolytic treatment consisted of allowing portions of the materials, mentioned above, to stand in an aqueous 0.5 *M* $KHSO_4$ solution at 47°C. under controlled conditions for increasing lengths of time. At intervals, small samples were withdrawn and converted into their nitrates by methods described in one of our previous studies (*3*). Each sample, representing a certain state of hydrolytic degradation and, hence, a member of a polyhomologous series, was then fractionated by the fractional precipitation technique, as described earlier (*3*). From the various fractions thus obtained, those having D.P.'s within a suitable range (i.e., between about 150 and 1300†) were selected for the $K_m$ constant determinations. As is seen from equation (2), these determinations comprised those of $\eta_{sp}$ and $M$.

Weighed amounts of the selected fractions were dissolved in known volumes of C.P. acetone. Portions were removed with a pipet and diluted with acetone to the desired concentration. These diluted solutions were then used for both the viscosity and the osmotic pressure measurements.

The viscosity measurements were carried out in the manner described earlier (*3*). The kinetic energy correction which was applied to the readings required a reduction of the measured value by 1.7%.

The specific viscosities ($\eta_{sp}$) may be converted into intrinsic viscosities [$\eta$] by the use of Staudinger's improved equation [(*7*); see also Mark in (*12*)]:

$$\lim_{c \to 0} (\eta_{sp}/c) = [\eta] = K_m \times M \qquad (3)$$

This requires the determination of $\eta_{sp}$ at various concentrations with subsequent extrapolation to zero concentration. The intrinsic viscosities also may be calculated by making use of the relationship:

$$[\eta] = (\eta_{sp}/c)/(1 + K_1\eta_{sp}) \qquad (4)$$

which was arrived at independently by Huggins (*8*) and by Schulz and Blasche (*9*). In equation (4), $K_1$ is a constant characteristic of a given solute-solvent system. For cellulose nitrate in acetone, Schulz and Blasche found $K_1$ to be 0.315.

In the present study, the conversion was made by using equation (4). Control measurements showed that the intrinsic viscosities thus calculated checked fairly well with those which were found by determining the specific viscosity at different concentrations with subsequent extrapolation to zero concentration and use of equation (3).

For determining the osmotic pressure of the nitrates, the osmometer as described by Zimm and Meyerson

**Table III. Intrinsic Viscosity and Osmotic Pressure of Cellulose Nitrates from Mitscherlich (Spruce) and Semichemical Aspen Pulps in Acetone**

| *Intrinsic viscosity* | *Osmotic measurements* | | |
|---|---|---|---|
| | c, *g./l.* | p, *mm.* (*acetone*) | p/c |
| | Mitscherlich Pulp (Spruce) | | |
| 1.198 | 5.45 | 17.5 | 3.21 |
| | 3.6 | 8.65 | 2.40 |
| | 2.92 | 6.4 | 2.20 |
| | 0 | .. | 1.06 |
| 0.852 | 5.15 | 19.6 | 3.80 |
| | 3.66 | 10.9 | 3.0 |
| | 1.75 | 4.0 | 2.30 |
| | 0 | .. | 1.53 |
| 0.396 | 3.4 | 16.5 | 4.85 |
| | 2.1 | 8.8 | 4.2 |
| | 1.2 | 4.6 | 3.8 |
| | 0 | .. | 3.25 |
| 0.268 | 3.75 | 25.4 | 6.77 |
| | 2.8 | 17.9 | 6.38 |
| | 1.55 | 8.95 | 5.78 |
| | 0 | .. | 5.10 |
| 0.200 | 4.0 | 16.5 | 4.85 |
| | 2.0 | 8.8 | 4.2 |
| | 1.0 | 4.6 | 3.8 |
| | 0 | .. | 3.25 |
| | Semichemical Aspen Pulp | | |
| 0.740 | 3.30 | 10.9 | 3.3 |
| | 1.65 | 4.2 | 2.55 |
| | 0 | .. | 1.73 |
| 0.314 | 3.5 | 19.9 | 5.7 |
| | 2.3 | 11.9 | 5.2 |
| | 1.4 | 6.7 | 4.8 |
| | 0 | .. | 4.2 |
| 0.176 | 3.55 | 31.6 | 8.9 |
| | 2.55 | 21.4 | 8.4 |
| | 1.75 | 14.2 | 8.1 |
| | 0 | .. | 7.4 |

* Produced by pulping with neutral sulphite (pentosan, 20.5%; lignin, 10.2%; average D.P., 2000).

† For these D.P. determinations, the $K_m$ value of $11 \times 10^{-4}$, as established by Staudinger and co-workers, was used.

(*10*) was used. The membrane consisted of a cellophane sheet (not waterproofed) which, according to Wagner (*11*), is more uniform than denitrated collodion. For the study reported here, it was supplied by du Pont de Nemours & Co. The membranes cut from the sheet were stored in distilled water to which some formaldehyde had been added to prevent bacterial attack. They were then conditioned for use by washing with distilled water (to remove all formaldehyde) and gradually displacing the water with acetone. For details about this procedure, see also Wagner (*12*).

The desired number of osmometers were placed in large test tubes containing the solvent (acetone), and the tubes were kept in a temperature-controlled water bath at 20 ± 0.02°C. When equilibrium was established, which took from 1 to 3 days, depending upon the concentration and the D.P. range of the cellulose nitrate fraction under investigation, the difference in level of the menisci in the measuring and the reference capillaries of the osmometer (determined to ±0.1 mm. with a cathetometer) was the osmotic head.

The relationship between molecular weight and osmotic pressure for high polymers has been more recently reviewed by various investigators—e.g., Flory (*13*), Huggins (*14*), Spurlin (*15*), and Fuoss and Mead (*16*). On the basis of these studies, the molecular weight of the polymer under investigation may be derived from the following equation:

$$\lim_{c \to 0} (p/c) = RT/M \qquad (5)$$

in which $c$ is the concentration of the solute in grams per liter; $p$, the osmotic pressure; $T$, the absolute temperature; $R$, the gas constant, and $M$, the molecular weight to be found. As is seen from equation (5), the osmotic pressure is determined at different concentrations and subsequently extrapolated to zero concentration by plotting $(p/c)$ against $c$.

The results are listed in Table II for the cotton nitrate and in Table III for the two wood pulp nitrates. In the case of the cotton nitrate, the selected fractions ranged between D.P.'s of about 1300 and 170, in the case of the Mitscherlich pulp between about 1050 and 170, and in that of the semichemical aspen pulp between about 650 and 150‡.

The final results are listed in Table IV. The D.P. values were obtained by dividing the osmotic molecular weight by 279—i.e., the molecular weight of the individual unit of the cellulose nitrate chain with a nitrogen content of 13.0 and 13.2%. The $K_m$ values were obtained by dividing the intrinsic viscosities by the D.P.'s.

It will be noticed from Table IV that the $K_m$ values in all three cases are fairly constant, although the D.P.'s vary over quite wide ranges. For this reason, one would feel justified in using the $K_m$ constants found here, not only for the medium and low D.P. materials, but also for the fractions with molecular weights above the highest and below the lowest values shown in Table IV.

The average value of $9.6 \times 10^{-4}$ for hydrolyzed cotton checks fairly well with Schulz and Husemann's values, if their data are calculated in the manner described above. This recalculation yields a value of $9.4 \times 10^{-4}$. Likewise, the value listed in Table IV is perhaps not too far from that reported by Blaker, Badger, and Noyes (*2*) ($8.9 \times 10^{-4}$ for a cotton nitrate having a nitrogen content of 13.1%). Wannow and Thormann (*17*) found for the trinitrate of kier-boiled and bleached cotton a value of $10.2 \times 10^{-4} \pm 4\%$.

‡ The plots of $p/c$ against $t/c$ are reproduced in Leif Jörgensen's doctoral dissertation, p. 55. Oslo, Emil Mostue A/S, 1950.

**Table IV. $K_m$ Constants as Derived from Intrinsic Viscosity and Osmotic Pressure Data for Various Cellulosic Materials**

| *Material* | *Intrinsic viscosity* | *D.P.$_s$* | $K_m \times 10^{-4}$ | *Average value of* $K_m \times 10^{-4}$ |
|---|---|---|---|---|
| Cotton | 1.210 | 1310 | 9.20 | |
| | 0.912 | 945 | 9.68 | |
| | 0.664 | 680 | 9.75 | |
| | 0.270 | 270 | 10.0 | |
| | 0.162 | 172 | 9.40 | 9.6 |
| Mitscherlich (spruce) pulp | 1.198 | 1060 | 11.30 | |
| | 0.852 | 735 | 11.59 | |
| | 0.396 | 348 | 11.35 | |
| | 0.268 | 222 | 12.04 | |
| | 0.200 | 168 | 11.88 | 11.6 |
| Semichemical aspen pulp | 0.740 | 640 | 11.58 | |
| | 0.314 | 268 | 11.73 | |
| | 0.176 | 152 | 11.55 | 11.6 |

That the $K_m$ value is different for cotton on the one hand and the two wood pulps on the other, in spite of the fact that all three cellulosic materials were subjected to the same acid hydrolysis (prior to nitration), would seem to indicate that an original difference exists which is not eliminated by such treatment. In this connection, it might be significant that wood pulps possess higher carboxyl contents than cotton.

Zapf (*18*) has explained the difference in the $K_m$ values for different cellulosic materials by differences in polymolecularity. As we have found, Zapf also found the higher values for wood pulps as compared with cotton cellulose. However, his values for both types of cellulose are considerably higher than ours—a discrepancy which for a satisfactory explanation would seem to require further experimental study.

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RECEIVED Aug. 30, 1951.

# Particle Structure and Flow Properties of Coating Clays

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**Data on the flow properties of clay-starch coating colors at relatively high solids contents are presented together with current information as to the structure of clay particles of various size. The effect of particle size and shape upon flow properties is shown to be such that the fine particle size fractions are particularly suitable for the preparation of high solids coating colors for roll application.**

A NUMBER of papers directed toward the structure of clays and their flow characteristics in aqueous suspension, and toward the rheology of complete coating colors, have been presented during recent years. Information dealing with coating colors is relatively the less complete as a result of the comparative complexity of these systems. It is the object of the present paper to present some of the more recent information relating to the nature and structure of kaolin clays and some experimental data regarding the flow characteristics of coating colors prepared from such clays.

The field is a broad one, and this discussion is by no means represented as covering more than a small segment of it. Attention will be directed primarily to coating colors having relatively high-solids contents, and those whose only mineral ingredient is clay and whose adhesive is starch.

The subjects of particle structure of clay, the nature of flocculation and deflocculation and their significance with respect to flow characteristics were discussed by Asdell (*1*) at the meeting of the TAPPI Coating Group a few years ago. The platelike structure of kaolinite particles was referred to in this paper. Recent work, notably by Woodward and Lyons (*2*), has demonstrated that it is primarily in the smaller particle size range that the clay particles are almost invariably single crystal plates. Figures 1 and 2 are electron micrographs of such single-plate crystals published by East (*3*). It can be seen that the crystals are in the form of more or less imperfect hexagons. Those in these pictures are of the order of 1 mu or less in diameter. Figure 3 shows clay particles predominantly in the range of particle sizes below 0.2 mu. The spheres are particles of latex with a diameter of 0.26 mu. While in this case, as contrasted with the first two photomicrographs, the particles have clustered to a marked degree in the field of the microscope, it is still readily apparent that the single-plate structure prevails, and a number of nearly perfect hexagonal plates of the order of 0.1 mu in size are readily seen. The pictures of Figs. 1 and 2 were made using the relatively new vapor shadowing technique by means of which it has been possible to obtain a direct confirmation of previous estimates as to the thickness of the plates. This is on the average, of the order of one-twelfth of the larger dimensions, some evidence indicating that it tends to vary in the different ranges of particle size.

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Woodward and Lyons (*2*) have shown dramatically that most of the larger kaolinite particles, those with equivalent spherical diameters larger than about 2 mu, are not flat crystal plates, but stacks of plates laminated together. Such stacks exist in the deflocculated as well as the flocculated state, and we may thus conclude that the forces holding the plates together are of a different character than the attractive forces responsible for loose flocs which disperse readily after the fashion discussed by Asdell (*1*). For the most part, the shape of such particles can be regarded as irregular and there is no predominant ratio between dimensions along the various axes.

Such a difference in particle character, above and beyond a difference in size alone, might be expected to exert a profound influence upon both the behavior of the particles while in suspension and the properties of a finished coating containing them. Such is indeed the case. Whittaker (*4*) observed some ten years ago that clay-water systems containing predominantly clay particles larger than 2 mu equivalent spherical diameter tend to exhibit dilatancy. Compositions of a dilatant character are very well known to fail to apply properly in typical coating processes. Maloney (*5*) first called particular attention to the marked difference in gloss-imparting and hiding characteristics which are found at about this same dimension. The flat-plate kaolinite crystals, characteristic of the smaller particle size range, appear to be almost beyond question those best suited for advantageous use in many paper coating applications.

Contrary to the ideas suggested by a number of previous authors, recent data published by Van Wazer and Besmertnuk (*6*) imply that the phenomenon of deflocculation is not attributable to the exchangeable cations associated with the clay particles nor is the presence of free hydroxyl ions necessary. Their work with phosphates indicates that the effectiveness of a deflocculant increases as its anionic charge increases, and they present evidence that chemisorption of the anion of the deflocculant through formation of complexes with some of the surface silicon and aluminum atoms on the clay particle is necessary in order to have deflocculation. Their evidence with regard to the effect of exchangeable cations is not entirely convincing inasmuch as it is confined to monovalent ions. It has been shown by Asdell (*7*) that sodium hydroxide is quite equivalent to a polyphosphate in its ability to deflocculate providing that possible interfering ions are first removed from the clay surface or a small amount of a compound capable of rendering interfering ions inactive is employed with the sodium hydroxide. Commercial clays can and occasionally do contain interfering ions in sufficient quantities that the ability to render them ineffective through base exchange reactions or other mechanisms is an important characteristic of an effective deflocculating agent.

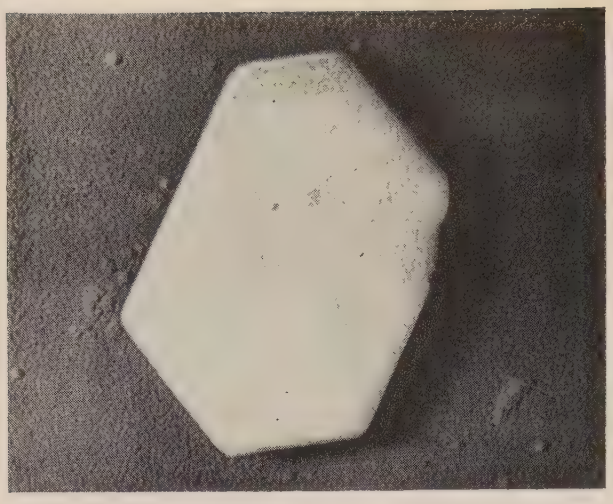

*Fig. 1*

Without dealing any more extensively with the mechanism of deflocculation, it is possible to form a mental picture of the two types of system represented by deflocculated and flocculated clay suspensions. In the case of the deflocculated suspension we have a system of small suspended particles which repel each other. The equilibrium condition of such a suspension would have the particles separated from each other as far as possible. Any disturbance or distortion of the system, or an increase in the rate of distortion, will be resisted since it will cause particles to approach each other more closely than under equilibrium conditions. At high concentrations the amount of distortion necessary to bring about mechanical interference between particles is not great. At lower concentrations the resistance to increasing rates of shear, or distortion, at least over a considerable range, may be so slight as to be unapparent and the suspension may appear to be a Newtonian liquid. Under no conditions should such a perfectly deflocculated suspension, with no other components present, exhibit true thixotropy or work softening although such suspensions do exhibit a type of anomalous flow reported by Van Wazer and Besmertnuk (*6*), and possibly earlier by Rossi (*8*), which can easily be confused with thixotropy.

Figure 4 is a rheogram prepared with a Hercules recording viscometer on such a system at the various indicated concentrations in terms of weight per cent. The chart shows the torque resulting from various rates of shear or strain (shown as revolutions per minute), which is adjustable. The changes in rate of shear during the preparation of these rheograms were purposely very slow, and, in each curve, shear at the maximum rate shown was continued until an equilibrium value of the torque appeared to be reached. The resistance of the system to increased distortion is apparent from the curvature of the graph at increasing rates of shear. This is the phenomenon frequently referred to as dilatancy but perhaps more properly designated as "shear-rate thickening" or "shear-rate blockage" since, as has been pointed out by Reiner (*9*), dilatancy refers to a change of volume caused by shear and not to a relation between shear and shearing stress. The unexplained phenomenon described by Van Wazer and Besmertnuk (*6*) and christened "tachypyknosis" is evident in the tremendous reduction in torque when shear is continued as a constant rate. The clay from

**Table I**

| *Deflocculant Added, %* | *Brookfield Viscosity* | *—Plastic Viscosity at— 525 r.p.m.* | *1050 r.p.m.* | *Leveling Index* |
|---|---|---|---|---|
| 0.15 | 48,700 (12 r.p.m.) | 2.38 | 1.96 | 0.31 |
| 0.20 | 18,400 (30 r.p.m.) | 1.77 | 1.45 | 0.31 |
| 0.30 | 1,360 (60 r.p.m.) | 1.21 | 1.03 | 0.24 |
| 0.40 | 1,700 (60 r.p.m.) | 1.25 | 1.05 | 0.26 |
| 0.60 | 1,680 (60 r.p.m.) | 1.04 | 0.89 | 0.23 |

which the rheograms of Fig. 4 were prepared consists almost entirely of particles less than about 4 mu in equivalent spherical diameter, over 90% by weight being less than 2 mu, so that it obviously is composed predominantly of the type of single-plate crystals shown in Figs. 1 and 2. Figure 5 is another set of rheograms on a similar series of suspensions of the same clay, but with the changes in rate of shear made at a steady, but higher rate and with no delay at the maximum shearing rate to permit tachypyknosis. It is fairly apparent from the similarity of the curves at increasing shear rates that, unlike tachypyknosis, shear-rate thickening and shear-rate blockage are not related to the rate of acceleration of shear.

The abruptness with which a condition of shear-rate blockage is reached appears to be much greater, and the rates of shear at which it takes place much lower, when the content of colloidal matter in suspension is reduced or eliminated. Figure 6 shows rheograms prepared in the same way as those of Fig. 5. The clay in this case was identical in its maximum particle size, but was refractionated in a high-speed centrifuge. The effluent from the centrifuge contained the finest colloidal and near-colloidal particles which had not been settled out of suspension by the centrifugal forces involved. Under the conditions of this experiment approximately 13% of the clay by weight, representing the finest particles, was removed. The clay used in making the rheograms of Fig. 6 was the 87% fraction remaining—from which some extreme fines had been removed. The exceedingly abrupt blockage at a critical rate of shear is obvious in the slurries with maximum concentration. Repeat runs on the same slurry gave rheograms which superimposed to near perfection. The nature of the portion of the curve representing decreasing rates of shear is puzzling, and at this writing is subject to some uncertainty as to whether

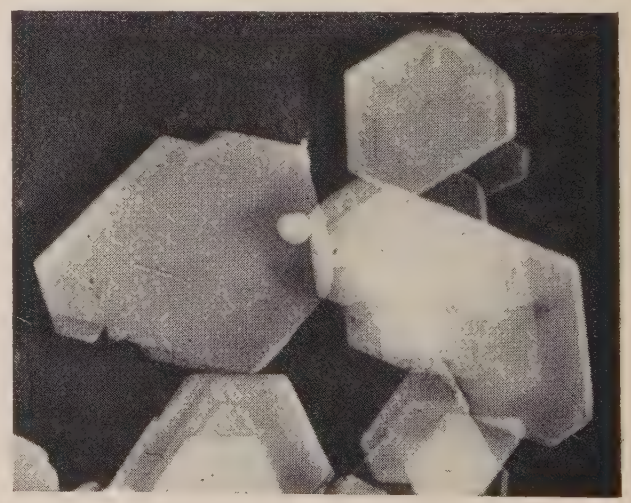

*Fig. 2*

**Table II**

| Deflocculant Added, % | Brookfield Viscosity | Plastic Viscosity at 525 r.p.m. | Plastic Viscosity at 1050 r.p.m. | Leveling Index |
|---|---|---|---|---|
| 0.15 | 5250 (60 r.p.m.) | 2.37 | 1.96 | 0.30 |
| 0.20 | 4950 (60 r.p.m.) | 1.76 | 1.49 | 0.27 |
| 0.30 | 1830 (60 r.p.m.) | 1.33 | 1.09 | 0.31 |
| 0.40 | 4000 (60 r.p.m.) | 1.52 | 1.23 | 0.35 |
| 0.60 | 4300 (60 r.p.m.) | 1.52 | 1.25 | 0.32 |

it represents a true picture of the behavior of the suspension, perhaps another example of tachypyknosis, or came about through some unexplained characteristic of the instrument. This "down curve" too, however, was capable of repetition. The instrument bob used in preparing Fig. 6 was not the same as that of Fig. 5, so that the instrument constants and the scale of shear rates do not coincide. Actually, the clay from which 13% of extreme fines had been removed was not more fluid than the starting clay at 71% solids, as might appear to be the case from a casual glance. Figure 7, made with the same clay as Fig. 6, but with the instrumental arrangement corresponding to Fig. 5, clearly shows the reverse.

The type of flow shown in the rheograms of Figs. 4 to 7 is characteristic of high-solids clay-water systems, but is definitely, of course, the type which is not wanted in a coating color. Yet, although the examples shown may be extreme and were chosen to show exaggerated shear-rate thickening, the nature of a completely deflocculated clay-water system is such that some tendency toward this condition must be present for the condition favoring maximum fluidity is logically that the suspension be at rest.

The completed coating color, in order to obtain satisfactory coating operation on a roll-type coater, must not exhibit the type of flow characteristic shown in Figs. 4 to 7, but must constitute a system in which attractive forces between suspended particles exist. Such a system, at rest, reaches a stable equilibrium in which an internal structure of some degree of rigidity may be formed. When the system is sheared, or distorted, disruption of bonds forming the internal structure takes place. As the rate of shear is increased the destruction of such bonds becomes more complete, and the resistance to shear is correspondingly lessened. Thus slight increases in shearing force produce relatively large increases in rate of shear. Smith and his coworkers (*10*) have discussed the requirements of a satisfactory coating color from the standpoint of rheo-

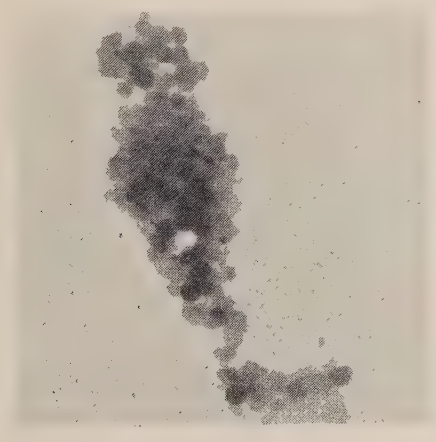

*Fig. 3*

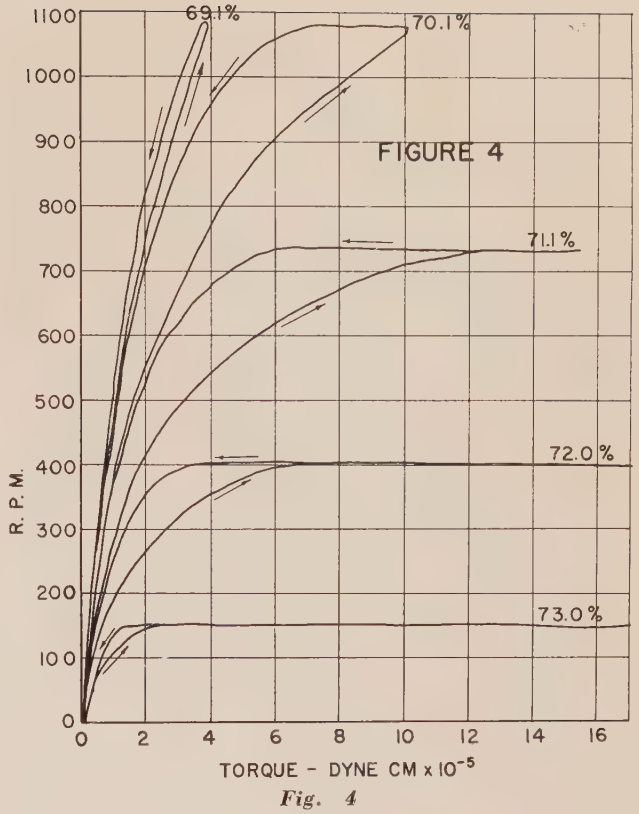


*Fig. 4*

logical properties and introduced the concept of a "leveling index" as a measure of the tendency of a coating color to cause a surface pattern on the coated sheet. This leveling index is the ratio of the coefficient of thixotropic breakdown to the plastic viscosity, and for a given set of operating conditions there appears to be a minimum leveling index below which coatings will not apply satisfactorily.

One of the factors exerting a profound influence upon the flow properties of a coating color will obviously be the extent to which the clay particles are present as deflocculated individual particles or as flocs. Table I shows some rheological data on a coating color of a fairly typical composition. Like those on which data will be presented later in this discussion, it had a total solids of 60% by weight. The adhesive was a low-viscosity chlorinated starch and the weight-ratio of starch to clay was 12 to 100. In this case the clay used was of the type represented by Figs. 4 and 5, over 90% of which consisted of particles less than 2 mu in equivalent spherical diameter. Tetrasodium pyrophosphate was employed as the deflocculant at the indicated percentages in terms of the weight of clay.

It is apparent from the Brookfield viscosity data, at relatively low (and unfortunately nonconstant) shear rates, that the condition of the suspensions containing less than 0.3% of added deflocculant did not exhibit thorough deflocculation. Let us see the situation at higher rates of shear, more nearly simulating the shearing conditions in a coating nip. The plastic viscosity of the imperfectly deflocculated colors even at 1050

**Table III**

| Clay | Brookfield Viscosity | Plastic Viscosity at 525 r.p.m. | Plastic Viscosity at 1050 r.p.m. | Leveling Index |
|---|---|---|---|---|
| I | 1660 (60 r.p.m.) | 1.63 | 1.39 | 0.25 |
| II | 970 (60 r.p.m.) | 2.21 | 2.01 | 0.19 |

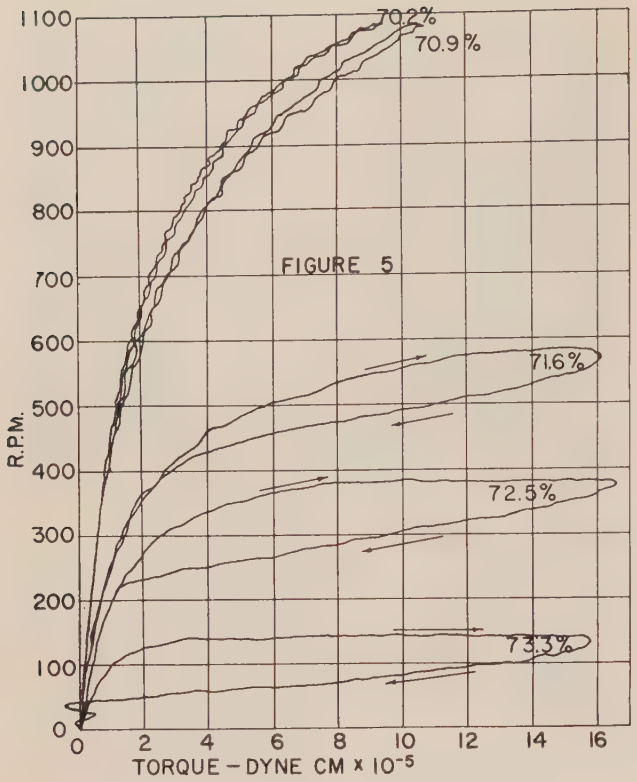


*Fig. 5*

r.p.m., corresponding to a shear rate in this case of 4300 seconds$^{-1}$, was noticeably higher than for the colors containing adequate deflocculating agent, but as compared with the low shear-rate the differences are not great. The tremendous resistance to shear of these imperfectly deflocculated colors was, then, largely thixotropic. This is further shown by the tabulated values of leveling index which indicate that these poorly deflocculated colors might actually be expected to be operable in many high-speed coating operations if their flow properties permitted their handling, including the manipulations prior to the actual coating step. The well-deflocculated colors, on the other hand, with the particular type and quantity of adhesive used, were free-flowing but showed too little thixotropy in spite of the fineness of the clay fraction to insure satisfactory coating in some operations, as indicated by the values of the leveling index. A frequently used criterion with respect to this value is that it should equal or exceed 0.3 to insure a satisfactory pattern-free coating.

The desired condition, then, is one combining to as great an extent as possible the free-flowing characteristics associated with thorough deflocculation with the thixotropic behavior exhibited when the clay is at least partially flocculated. Successful coating formulation achieves this by the use of components which contribute primarily to the thixotropy of the complete color. Much can be accomplished in this direction by careful selection of the adhesive component of the color. The use of fine particle-size clays is helpful although, as shown in Table I, not an automatic assurance that

**Table IV**

| Clay | Brookfield Viscosity | Plastic Viscosity at 525 r.p.m. | Plastic Viscosity at 1050 r.p.m | Leveling Index |
|---|---|---|---|---|
| I | 5050 (60 r.p.m.) | 2.09 | 1.69 | 0.34 |
| II | 6200 (60 r.p.m.) | 3.03 | 2.60 | 0.25 |

**Table V**

| Clay | Brookfield Viscosity | Plastic Viscosity at 525 r.p.m. | Plastic Viscosity at 1050 r.p.m. | Leveling Index |
|---|---|---|---|---|
| A | 1800 (60 r.p.m.) | 1.43 | 1.22 | 0.25 |
| B | 1660 (60 r.p.m.) | 1.16 | 0.99 | 0.24 |
| C | 1600 (60 r.p.m.) | 1.09 | 0.95 | 0.22 |

high leveling indices will result despite the nature of the remainder of the coating color. Additives such as soaps are frequently useful. Table II shows data for a series of colors identical with those of Table I except that their flow properties were modified by the addition of a small percentage of a soap.

With the exception of the colors deficient in deflocculating agent, where the alkali added in the form of soap may have furthered deflocculation to some degree, it can be seen that the viscosities at either low or high shear rates tend to be increased, but not to a prohibitive degree. The thixotropy has been enhanced, notably in the cases where deflocculation was good, as evidenced by the generally high values for leveling index. All of these colors are apparently sufficiently thixotropic to apply properly, the well-deflocculated ones preserving their advantage in the generally lower level of plastic viscosity.

A clay of coarser particle size, consisting predominantly of "stacks" rather than single crystal plates, tends to be very fluid at low-solids contents and to exhibit low viscosity even at relatively high-solids contents if the rate of shear is low. It is particularly subject to shear-rate thickening and sudden shear-rate blockage of the type shown in Fig. 6 in high-solids aqueous suspensions. Figure 8 shows the particle-size distributions of two clays, each with about the same maximum particle size, but with clay I prepared so as to contain approximately 80% by weight of the minus 2-mu single-plate crystals and clay II prepared

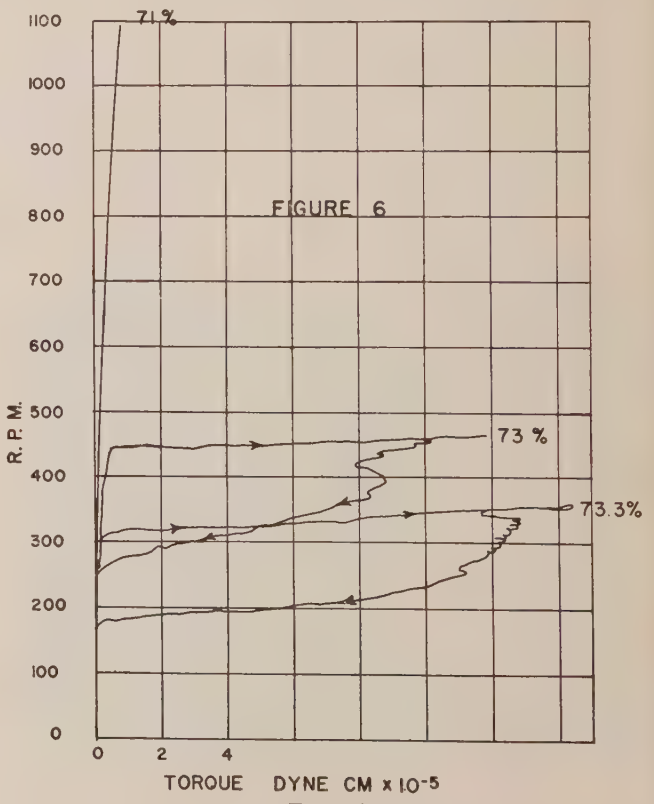


*Fig. 6*

**Table VI**

| Clay | Brookfield Viscosity | Plastic Viscosity at 525 r.p.m. | Plastic Viscosity at 1050 r.p.m. | Leveling Index |
|---|---|---|---|---|
| A | 5700 (60 r.p.m.) | 1.79 | 1.48 | 0.30 |
| B | 5700 (60 r.p.m.) | 1.69 | 1.37 | 0.32 |
| C | 5250 (60 r.p.m.) | 1.66 | 1.40 | 0.30 |

so that the percentage of such particles is only 46%. Table III gives rheological data on 60% solids coating colors prepared from these clays and Table IV gives similar data for identical colors modified with added soap.

It is apparent that the clay deficient in the fine platelike crystals is the more fluid at low shear rates but that it exhibits none, or at least less, of the thixotropic breakdown which leads to low-viscosity readings at high shear rates and to a satisfactory leveling index. The addition of soap introduces enough thixotropy to raise the leveling index, although not to the 0.3 level, and the high-shear plastic viscosity remains about 60% higher than for the similar fraction—in the sense of maximum particle size—containing the greater portion of minus 2-mu particles and about $2^1/_2$ times that for the finer clay fraction of Table II, for an identical coating formulation.

Clays fractionated so as to consist essentially of the desirable single-plate crystals under about 2 mu in diameter can be prepared so as to contain varying amounts of the colloidal and the extremely fine near-colloidal particles in the submicron range. The particles in this range, too, exhibit their influence on the working properties of coating colors. Tables V and VI present rheological data on colors prepared from three such clays. Clay A can be regarded as the starting material—its fractionation was such that it had a maximum particle size of approximately 4 mu equivalent spherical diameter, substantially over 90% under 2 mu, and a quantity of colloidal or nearly colloidal particles consistent with the character of the low-viscosity crude from which it was prepared. Clay B was prepared by removing about 4% by weight of the extreme fines from clay A, and clay C was prepared by a similar process except the quantity removed was 13%.

Thus in these clays there is a consistent absence of large stacklike particles in every case but the clays differ in their colloidal content. Table V is based upon coating colors with no soap content. It is obvious that the removal of colloidal material causes a stepwise reduction in viscosity—evident over the entire range of shear rates studied. The thixotropy, however, decreases simultaneously and even to a greater degree, so that the leveling index tends somewhat downward.

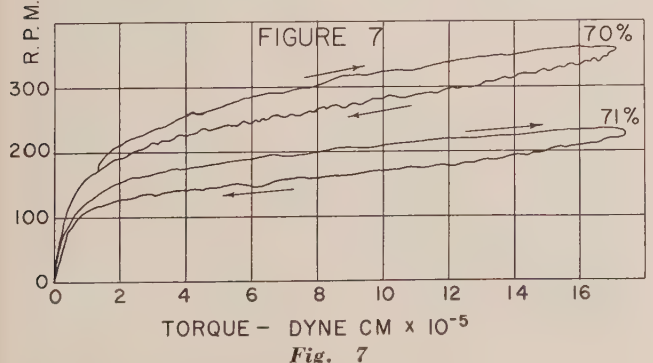

*Fig. 7*

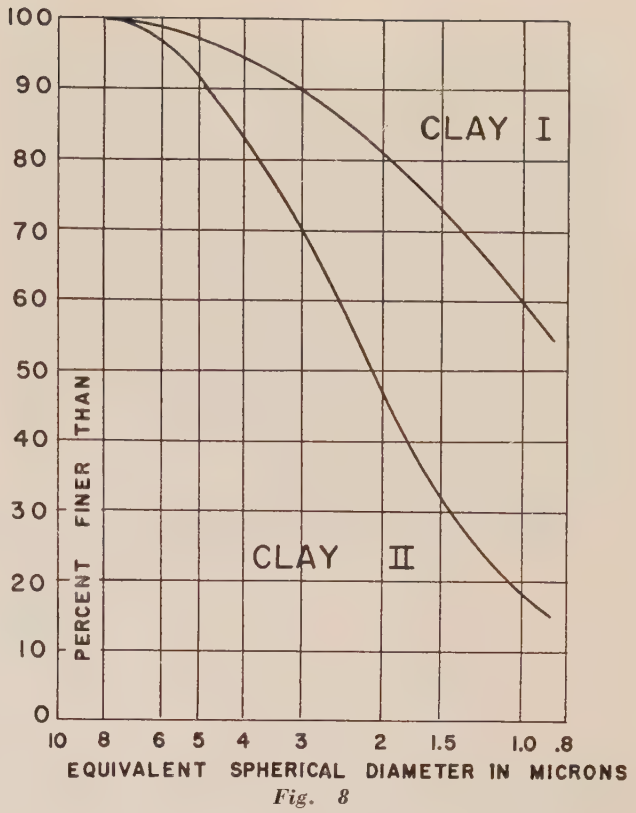

*Fig. 8*

As noted above the use of a soap can compensate for the low thixotropy. Table VI shows the identical coating colors formulated with a small amount of soap. It can be easily seen that the leveling index is raised to an adequate level, and that to a slight degree the viscosity reduction obtained by removal of colloidal matter is retained.

The viscosity reduction attributable to the removal of extreme fines is even more striking in the case of coating colors prepared by enzyme conversion of the starch in the presence of the clay. This may be an indication that the colloidal content of the clay tends to interfere with enzyme conversion, perhaps by adsorption of the enzyme. Table VII shows data on the same clay A and clay B of the two preceding tables—clay B being the same as A except for the removal of 4% of extreme fines. The coating colors in this case were at 60% solids and contained 17.6 grams of starch per 100 grams of clay, the starch having been enzyme converted in the presence of the clay. Unfortunately no high-shear viscosity data are available, and we thus cannot calculate leveling indices. The reduction in viscosity over the entire Brookfield range is, however, very material. Furthermore, the ratio between viscosity values at 100 r.p.m. and at 10 r.p.m. is nearly enough constant to indicate that the decrease in thixotropy due to removal of colloidal clay is not going to seriously impair the leveling characteristics of the color.

In conclusion, it can be shown that there is a difference in character, as well as in size, between clay particles above or below a particle size generally in the neighborhood of two microns. To a considerable

**Table VII**

| Clay | Brookfield Viscosity 10 r.p.m. | 20 r.p.m. | 50 r.p.m. | 100 r.p.m. |
|---|---|---|---|---|
| A | 9920 | 6060 | 3344 | 2244 |
| B | 3960 | 2480 | 1420 | 990 |

degree the flow properties of clay-water systems and of high-solids coating colors can be shown to have a relation to the respective quantities of the two types of particle present and to the quantity of extremely fine colloidal or near-colloidal clay particles in the system. The relatively fine particles have long been known to impart desirable qualities to the finished sheet to the maximum extent, and particles of this order are also extremely desirable from the standpoint of application properties of the coating color.


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Received June 19, 1951. Presented at the Second Coating Conference sponsored by the Technical Association of the Pulp and Paper Industry, Boston, Mass., April 18–20, 1951.


# Use and Maintenance of Steel Windows in Pulp and Paper Mills


K. S. FRAZIER



**This article indicates the method of repair maintenance of steel windows in paper mills and buildings where high humidities prevail. Replacement is advised as more economical in most cases of severe corrosion. Selection of windows and correct installation details are shown to lengthen the useful expectancy of steel windows. Surface protection in the form of scheduled maintenance is compared with the more permanent protection now available in hot-dip galvanizing. Illustrations have been selected to assist and clarify the text.**


It is the author's purpose to recommend with reference to the maintenance of steel windows and help crystallize the importance of protective maintenance. This will cover maintenance repair and replacement, installation details, selection of materials, and surface protection. It will cover in some detail the value of hot-dip galvanizing of steel windows for use in paper mills and particularly in buildings of high humidity.

It has been our privilege to contact groundwood, soda, sulphite, sulphate, and semichemical mills over a period of many years where we could talk to maintenance men and see the conditions firsthand under which steel windows should remain in good condition. We have seen good installations and poor installations. We have observed organized maintenance and careless maintenance and noted their relationships to the useful life of steel windows.

Normal atmospheres are found in offices, power houses, and warehouses of paper mills. Some humidity is found in the wood or chip mills. Periodic or almost continuous alkaline or acid condition with high humidity is to be found in digester rooms. Bleachers produce moist chlorine vapors, and the beaters create high humidities. The highest humidities are found in the machine rooms with the fourdriniers where tremendous quantities of water are extracted and vaporized from the pulp. Where make-up liquids are prepared on the premises for sulphite mills, outside atmospheres in the vicinity are often laden with acid vapor. All of these conditions increase the maintenance problem. One engineer stated that every steel window that came into the plant was given several coats of a well-advertised protection before installation. Then he added, "Of course, nearly every job is so rushed that we don't find time to do this."

It seems fundamental that the protection of equipment from corrosion is less costly than continuous repair maintenance or early replacement; however, the requirement of repair and replacement does quite generally prevail and cannot be ignored. General Knudsen once said: " 'status quo' is just another name for 'the mess we are in,' " and that just about covers what we are sometimes called upon to evaluate in maintenance.

Steel must be protected from the caustic atmospheres of soda mills and the caustic and acid atmospheres of sulphate mills and the acid atmosphere of the sulphite mills, and all of these are generally associated with extreme humidity.

This protection is mainly against the one natural enemy of steel which is rust. It is surprising how little is known about the formation of rust. The most generally accepted theory of rust formation stems from the fact that the surface of steel is not entirely homogeneous chemically and physically. Each little area then differs in electrical potential and in the presence of an electrolyte, such as acid or salt vapor, forms small storage batteries on the steel surface which cause the areas of higher potential to disintegrate and oxidize, forming rust. Without the presence of moisture the electrolytic potentials are inactive and no rust forms. From this you can readily see how important it is to keep moisture from the steel surface.

This can be accomplished in two ways. First, a good paint properly and often applied does a fine protective job. Second, hot-dip galvanizing does a much superior job.


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In a bulletin "Painting Steel" (*1*) from the U. S. Department of Commerce it is stated that there is no paint film today that is absolutely impervious to moisture. It then follows that the greater the humidity and the more contaminated the moisture, the greater becomes the maintenance problem where painting is used for protection.

## MAINTENANCE REPAIR

Let us look realistically for a moment at the problem of the maintenance of steel windows which have become, for any one of a number of reasons, corroded or damaged beyond usefulness. In many cases portions of these windows are still in good condition with the damage showing at the weathering around ventilators or toward the bottom of the windows. Many of these need only the replacement of one or two horizontal bars and perhaps the lower 1 foot 0 inch of vertical bars. If not buried in the masonry the defective bars may be cut out, after the lower glass lights are removed, and new bars fitted and welded in place. After repair, the whole unit should be thoroughly wire-brushed and given two coats of protective paint. The drawback to this work is the clearing of the opening to make imbedded bars accessible, the difficulty of obtaining the proper bars for replacement and the expense involved.

In normal times these bars can be obtained but due to existing pressure on manufacturers of steel windows to obtain sufficient steel to take care of production, only a limited tonnage of sections are available to steel window service companies who normally do this type of work.

It is found sometimes in buildings that steel windows have become distorted to the extent that ventilators will not close properly if at all. In practically every case of this kind it will be found that the head jambs and sills of the windows have been bedded solidly into the masonry and the small settlement of shifting of the building has caused the distortion. In checking the condition where windows were bowed we found that the piers between bays had settled a fraction of an inch. The curtain wall between bays not bearing a load had remained in place thus shortening the clear height for the windows. Rust forming under the sill bar will create a pressure upward with a similar resultant bowing of the window.

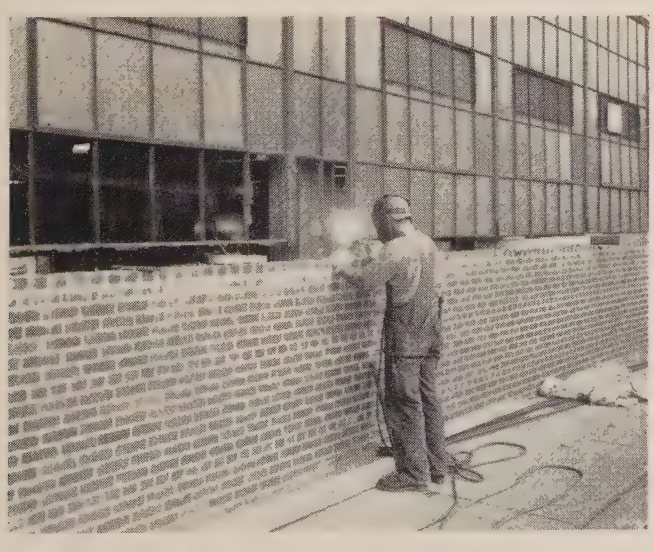

*Fig. 1. Replacing the sill bar*

*Fig. 2. Built-in units, damaged by trades*

For example, take a window 10 foot 0 inches high and reduce this height by only $^1/_{32}$ inch by outside pressure. The vertical bars of the window will be forced to bow 1 inch from their normal plane. If outside pressure reduces the opening $^3/_{32}$ inch, these bars will be forced to bow, usually outward, 2 inches. No ventilator could be closed tight where this condition exists. The remedy here is to remove the stone or cement sill, straighten the window, and replace the sill with proper freedom for the sill bar. The most satisfactory method is to remove the window from the opening and remove the glass from the window for this operation.

The costs of this type of repair will in many instances on careful analysis indicate the replacement of these units.

## MAINTENANCE REPLACEMENT

The influences of war periods change many things and the last war period emphasized the need for coordination of dimensions of building products. As a result of the modular coordination movement and the modern trend to wider glass lights, the dimensional design of all steel windows has been changed. Before this change, there were 30,000 types of windows cataloged for sale by the industry. W. C. Randall, Chief Engineer of the Detroit Steel Products Co., reported to the "Standard Modular Conference" (*2*), 500 to 600 types available in 1951. With all of its advantages there are handicaps, and the most annoying of these is probably the replacement of prewar units with units of the new design.

For a long time replacement units were custom built but the pressure of production and costs has ruled against this with most window fabricators excepting for quantities large enough for production runs. It seems advisable to use the new sizes wherever possible since units will be more economical and more readily available.

In multiple-unit openings where prewar sash was used this means only the proper selection of types and mullion width and the raising or lowering of the sill in its replacement.

In single-unit openings it adds the requirement of rebuilding the jamb or jambs or adjusting the openings with the less desirable jamb angles or plates.

Knowing the size of the opening to be filled, the sales

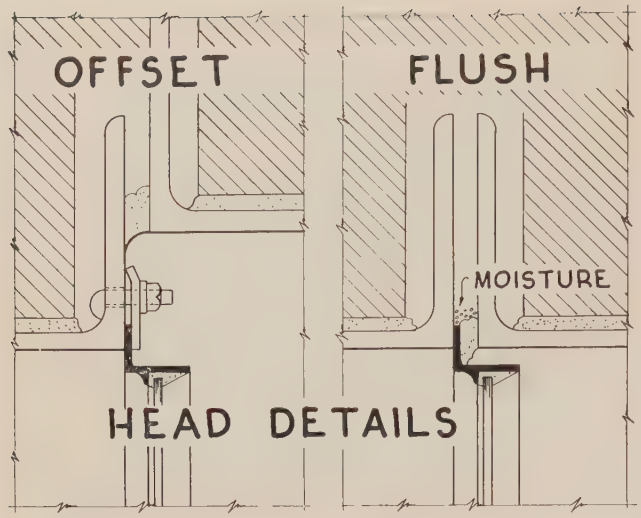


*Fig. 3. Comparative head details*

representative of the window manufacturer can help materially in the selection of proper types.

### INSTALLATION DETAILS

It is advisable on replacement or new work to prepare the openings in such a manner as to incur the least risk of unnecessary maintenance. Much research and study has been given to this problem, and all conclusions point to the advantages of prepared openings for steel windows. By this is meant an opening in which the window can be installed after the masonry is completed.

There are other items of advantage besides the protection of the window from masonry pressure distortion previously referred to.

If set after masonry is completed, the windows will not be used for scaffolding supports or ladders for which they are not designed. The windows will not be subject to the lime mortars or acid wash from the masonry work. The masonry work will in no case be held up for window delivery. Removal and replacement of damaged units is comparatively simple.

In spite of all of these advantages some contractors prefer to brick units in place but in no event should a sill be forced or poured tight against the sill section.

Most paper mill buildings are of masonry construction so that we can confine our installation details to this material. The head and jamb detail should be of the offset design since with a flush detail moisture has an opportunity to collect and remain in the masonry pocket around the leg of the window section. The offset lintel allows for the sill to be poured or placed before the windows are set and allows the window to be removed or repaired without destroying or removing the sill.

The sill detail offers the best opportunity for a corrosion condition if not properly installed.

Here it is found that a slip stone outside sill backed up inside with a stone or poured sill is the most satisfactory since in its placement a guaranteed freedom of the sill bar may be easily maintained.

In placing sills before installation of the windows, pockets should be left to receive anchor clips at mullion points. In the case of a poured sill here is one system used successfully. Pour alternate sections of the sill to window unit widths. Next cover the ends of the sill sections with a heavy paper rolled or folded at the point where the anchor pocket is required. Then pour the sections of sill between those poured first. This system produces a nice sill with thin expansion joints, and the pockets may be grouted in after anchor clips are in place.

### SELECTION OF MATERIALS

There are two groups of windows available, interchangeable as to size.

The industrial group of windows, with pivoted corner connections and combination sections around the ventilators, are rugged windows and may be obtained with pivoted or projected type ventilators.

By combination section is meant the use of two bars welded or riveted together to obtain proper weathering surfaces between window frame and ventilator.

The intermediate or solid casement section group of windows has welded corners and is classified in families with projected ventilators, side hung ventilators, or a combination of these two.

The solid casement section window costs slightly more but has a definite advantage where high humidities are found since it shows no fine crevices for moisture to collect in and remain to create rust.

Either type may be obtained hot-dip galvanized.

One efficient type of window has two ventilators. A two-pane high ventilator located near the top projects out, shielding the opening from rain while permitting the hotter upper air to escape. A one-pane high ventilator is located at the sill. The top of this ventilator projects in, forming a built-in wind guard which sheds rain to the outside and protects against direct drafts.

### SURFACE PROTECTION

The author has referred to hot-dip galvanized and bonderized steel windows since this product will minimize maintenance problems.

We have watched hot-dip galvanized windows as used in industry for 20 and 30 years with exceptionally good results and minimum maintenance requirement. An engineer remarked in referring to the galvanized sash which have been in his plant since 1933: "They don't seem to do a thing but sit there and take it. To us galvanizing seems to be the answer."

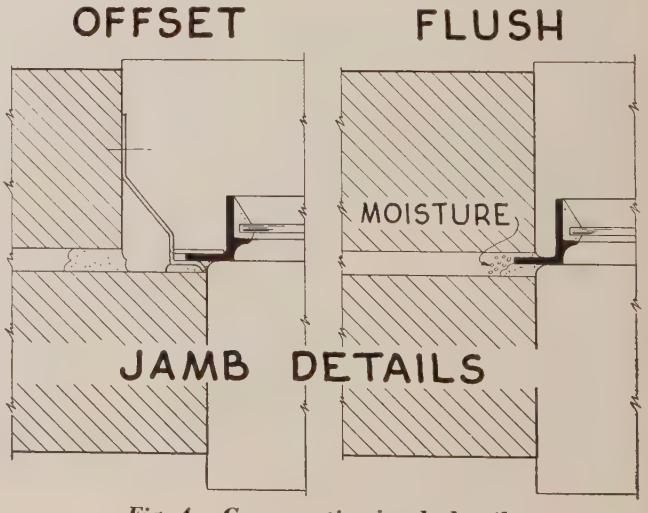


*Fig. 4. Comparative jamb details*

The hot-dip galvanizing of steel windows is obtained by the thorough cleaning of fabricated units from all grease, oils, scale, and rust, submerging it in molten zinc at a temperature of 850°F., allowing it to come to the temperature of the zinc bath, and then slowly withdrawing it. The full amount of accepted zinc is left on the surface in a smooth ductile coating having adherent qualities and substantial weight, guaranteeing a long lasting protection.

It is important in considering the maintenance-free life of this product that ferrous hardware, installation clips, screws, nuts, and bolts be given a protection coating equal to that of the windows, otherwise maintenance problems would begin with hardware breakdown. This protection is now possible due to developments in spin galvanizing for small parts. It is important that galvanizing be done after assembly of the frames so that all joint crevices are coated over with zinc.

Hot-dip galvanizing is a fascinating subject since it differs advantageously in many ways over nearly every other protective coating.

In this process we have a material that alloys to the base metal while submerged in the molten zinc to form a permanent bonding zinc iron with extreme corrosion resistant quality.

As the work is withdrawn from the bath the alloy layer is covered with a layer of almost pure ductile zinc which flows to a smooth uniform finish.

The sacrificial quality of zinc when used on a steel base is well established and places this material in a class by itself.

Every metal possesses an electrical potential so that when two different metals are placed together in the presence of an electrolyte such as salt or acid vapor there is set up a very small electric current flowing from and breaking down the metal with the greater potential.

Since zinc has a greater potential than iron, where a small opening is present in a zinc coating, the current will flow from the zinc to the iron breaking down the zinc to fill the opening which protects the iron by sacrificing itself.

The steel cannot corrode so long as there is a trace of zinc left on its surface.

This characteristic together with the extremely slow corrosion quality of zinc produces an economical long-lasting protection in a hot-dip galvanized coating.

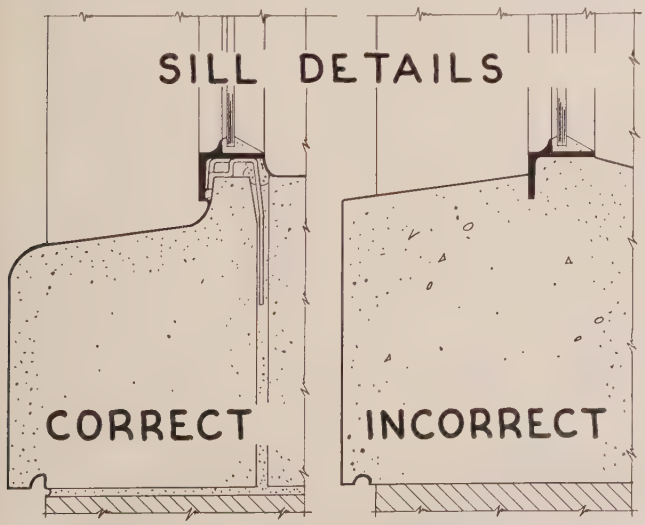


*Fig. 5. Comparative sill details*

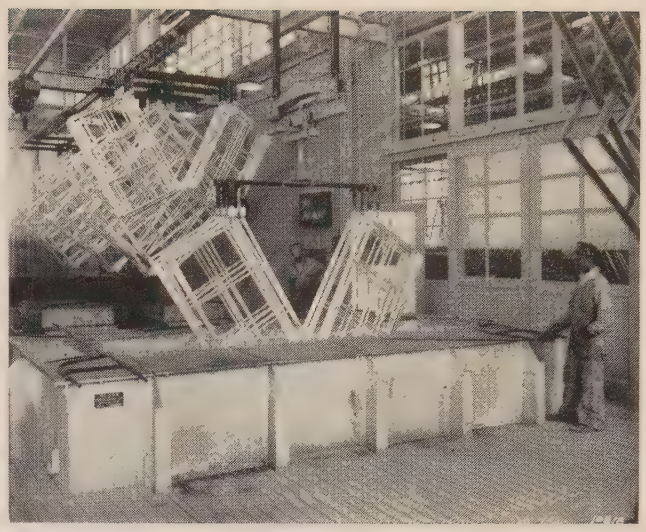

*Fig. 6. Galvanized sash withdrawn from the zinc bath*

An improvement in this quality coating is found in the phosphoric acid treatment such as bonderizing. Three things are accomplished in this treatment. It etches the surface slightly and brings about a chemical change that stabilizes the zinc surface materially slowing down zinc corrosion. It subdues the brilliant surface of new zinc to a uniform soft gray finish which is not only attractive but will remain substantially that way without darkening for many years.

It leaves a thin phosphate layer that creates an adhesive base for decorative paint if required.

In most areas initial painting will cost as much as hot-dip galvanizing which requires no paint except in extreme acid vapor conditions. Periodic repainting which constitutes a considerable maintenance item is normally saved with hot-dip galvanized windows, and the expensive wire-brushing of rusted areas can be eliminated.

Although hot-dip galvanizing will add many years of life to steel windows, in extreme acid atmospheres a periodic coating of bitumastic or acid-resistant paint will again protect the zinc that protects the steel and extend this life period indefinitely.

## SUMMATION

In general the maintenance problem with steel windows can be minimized by careful selection of materials, proper installation, and scheduled surface protection.

Our findings indicate that replacement is usually more economical and satisfactory than major repairs where corrosion has gained the advantage.

In new or replacement installations hot-dip galvanized bonderized windows will materially cut down the maintenance problem, and they should remain in good condition throughout the useful life of the building in which they are installed.

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Received June 25, 1951. Presented at the Engineering Conference sponsored by the Technical Association of the Pulp and Paper Industry, Savannah, Ga., Oct. 15–18, 1951.

# Characterization of Petroleum Waxes by Solvent-Fractionation Methods

F. H. MACLAREN

**Petroleum waxes, used primarily in the manufacture of protective wrappings for foods and confections, have been the subject of many published papers dealing with physical properties, crystal form, composition, and methods of manufacture. Study of melting-point distribution of these hydrocarbon mixtures is time-consuming because of the highly complex and closely related chemical composition. Application of specially developed laboratory solvent-fractionation procedures has been of considerable aid in showing melting-point distribution of petroleum waxes. These solvent-fractionation methods for characterization of commercial waxes show trends that can be related to known performance requirements in the wax-coating and laminating fields. Data obtained by one of the solvent-fractionation methods compare closely with those obtained by lengthy vacuum fractional distillation. While these solvent methods do not provide an ultimate chemical analysis, they do provide a rapid and reliable means of appraising waxes as to their melting-point distribution.**

PROTECTION of foods against loss of water vapor by use of waxed papers and cartons has been widely practiced for nearly fifty years. As shown by Herrman (*1*), petroleum waxes when present in a continuous film are efficient organic substances for preventing the transfer of water vapor. Until about 1926 coating of food wrappings was accomplished entirely by the use of crystalline paraffin waxes obtained from light paraffin distillates. The small production of waxes from petroleum residuums was used entirely for veterinary and pharmaceutical purposes in the form of petrolatums.

Expansion of oil refining in the 1920's included the construction of more lubricating-oil processing facilities, which in turn made residual waxes ("amorphous waxes") available for paper coating and laminating. However, the true worth of these residual waxes was not generally recognized, nor were their excellent properties utilized on a large scale until the packaging demands of a global war began to make themselves felt. Production of residual waxes rose from about 50 million pounds in 1942 to nearly 200 million pounds a year at the end of World War II.

Along with the rise in the use of residual waxes there has also been a steady increase in the use of waxes from heavy motor-oil distillates. These waxes, commonly referred to as motor-oil waxes, are similar to paraffin waxes obtained from light paraffin distillates, and have found increased use in packaging.

A large amount of research has been devoted to petroleum waxes, and many published papers have dealt with methods of manufacture, composition, crystal form, and physical properties. In addition, much work has been done on methods of appraisal of wax properties in relation to use as coating agents and laminants. In our laboratories, specially developed solvent-fractionation procedures have been of considerable worth in showing data on melting-point distribution of the components of petroleum waxes. Such data are of value in understanding the physical properties of waxes of importance in commercial applications. Use of these methods on petroleum waxes has simplified efforts toward characterization and classification of these highly complex and closely related materials. As a preface to the discussion of experimental work, a summary of petroleum wax classification, based primarily on source and manufacturing procedure, is presented.

**Table I. Comparison of Wax Properties**

| *Wax* | *Character* | *Carbons* | *Melting point,[a] °F.* | *Viscosity[b] SSU at 210°F.* | *Crystals* |
|---|---|---|---|---|---|
| Paraffin | Brittle | 18–56 | 122–140 | 40 | Plates |
| Motor oil | Brittle | 26–42 | 145–170 | 50 | Needles |
| Residual | Flexible | 36–70 | 145–175 | 65–110 | Small needles |
| Tank bottom | Hard | 40–70 | 180–200 | .. | Very small needles |

[a] ASTM number D 938-47 T.
[b] ASTM number D 88-44.

## CLASSIFICATION OF PETROLEUM WAXES

Petroleum waxes of commerce comprise a broad class of crystalline compounds ranging in chain length from about 18 to 70 carbons. Included in these hydrocarbons are not only straight-chain paraffins but also

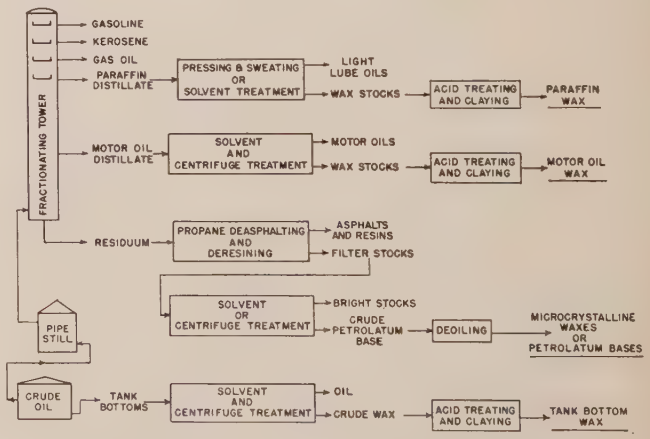


*Fig. 1. Refinery sources of petroleum waxes*

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branched-chain paraffins and even cyclic compounds. When properly refined, petroleum waxes are practically odorless, tasteless, and—under usual conditions of use—quite inert. They are easily melted and applied to paper in a thin film. Since these waxes are low-cost materials available in large quantity, wax consumption in food packaging has increased to more than a billion pounds per year.

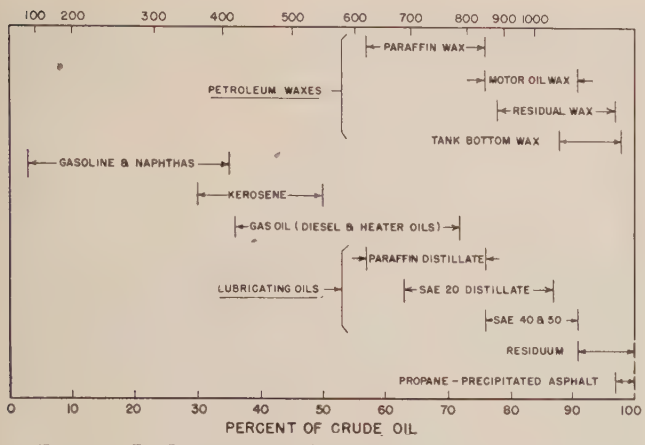


*Fig. 2. Boiling range of mid-continent petroleum products*

A simplified flow chart of the manufacture of petroleum waxes, similar to that of Clary (*2*), is shown in Fig. 1. Paraffin waxes are obtained from paraffin distillate; motor-oil waxes from the heavier distillate used to make motor oils; microcrystalline waxes and petrolatums from residuum, and tank-bottom waxes from the settlings in storage tanks containing wax-bearing crude oils. The boiling-point relationship of paraffin, motor oil, and residual waxes is diagrammed in Fig. 2. This chart, based on mid-continent crude oil,

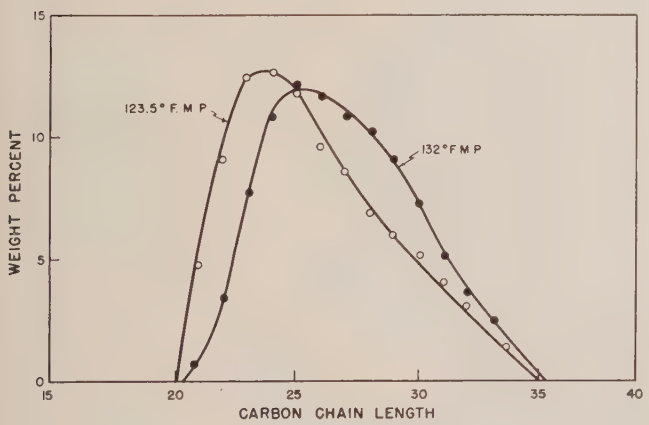


*Fig. 3. Distribution of normal paraffins in refined paraffin waxes*

also shows the boiling range of lubricating distillates with respect to gasolines and naphthas. The several waxes show markedly different properties, as shown in Table I; some of these can be explained in terms of composition and structure:

*Paraffin waxes*, if well refined, consist almost entirely of straight-chain paraffins, distributed as shown by the vacuum fractional distillation at 1-mm. pressure through a high-efficiency Stedman column illustrated in Fig. 3. Paraffin waxes have high tensile strength (*4*) and high shrinkage (*5*). In films they show relative dryness, that is, nonstickiness under pressure, or "blocking resistance," at temperatures up to 20°F. below the melting point, and show low adhesion or cohesion (sealing strength). The brittleness of paraffin waxes is usually ascribed to the shape and size of the straight-chain paraffin components, typified by large, thin plates (*6*), as shown in Fig. 4A. Brittleness causes paraffin wax films to rupture on creasing, folding or crumpling, but the resultant loss in waterproofness in normal packaging is small.

*Motor oil waxes* have properties dependent upon crude-oil source and refinery processing. They are, in general, much like paraffin waxes in brittleness and

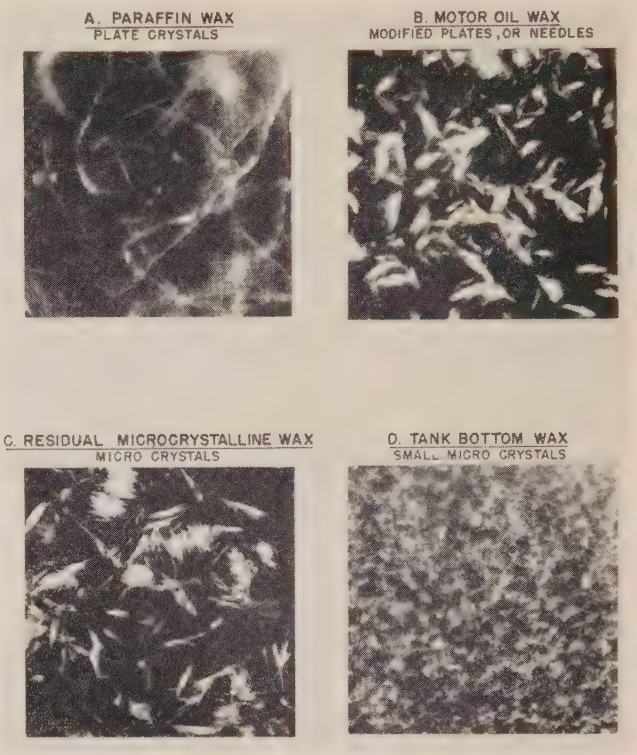


*Fig. 4. Crystal types of petroleum waxes (200 ×)*

shrinkage. Some motor-oil waxes are better in sealing strength and poorer in blocking resistance than paraffin waxes, apparently because of the presence of oil, low-melting branched-chain material, or cyclic compounds. On the other hand, some types contain more than 90% straight-chain paraffins, as determined by urea extraction (*7*), and are nearly as good in blocking resistance as refined paraffin waxes.

Motor-oil waxes crystallize in large needles, as shown in Fig. 4B. Crystal studies indicate that these needles are modified plates and are typical of the higher-melting straight-chain paraffins present. Plate crystals of paraffin waxes can be modified to the large needles by the addition of 5% or more of a high-melting residual wax.

*Microcrystalline waxes* (otherwise called *petrolatum bases*) of fairly low-oil content are residual waxes ob-

tained in the manufacture of bright stocks, as shown in Fig. 1. These waxes are typified by the micro or small-needle crystals illustrated in Fig. 4C. They contain up to 30% straight-chain paraffin; branched and ring compounds make up the remainder. Most waxes of the residual class are adhesive, plastic, and flexible, in part because of their oil content (*10*). Adhesiveness and low-temperature flexibility are important for satisfactory performance in laminating paper to paper, cellophane to paper, or metal foil to paper. The adhesive character of most residual waxes prevents use as surface coatings.

*Petrolatums* are unctuous apparent semisolid mixtures of microcrystalline waxes and oil. They exhibit marked plasticity and can be made to flow under low pressure. The physical nature of the crystalline hydrocarbons present in most microcrystalline waxes permits 1 part of wax to hold several parts of oil. This

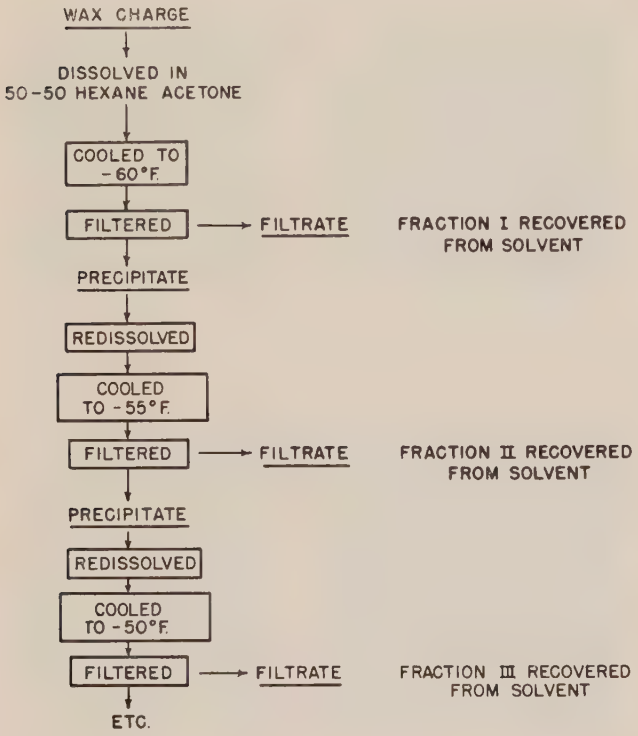


*Fig. 5. Hexane-acetone wax fractionation procedure*

wax-oil system has remarkable resistance at ordinary temperatures to syneresis or "bleeding" of oil, although resistance to bleeding varies considerably in commercial petrolatums.

*Tank-bottom waxes* are crystalline waxes obtained by processing the settlings from crude-oil storage, which contain the highest-melting waxes found in wax-bearing crude oils. These waxes usually show extremely small microcrystals, as illustrated in Fig. 4D, although some types show larger crystals intermediate between those designated C and D. Tank-bottom waxes contain large amounts of high-melting straight-chain paraffins and are much harder than residual microcrystalline waxes. Their hardness has made them of considerable value in commercial wax products like polishes. Oxidized tank-bottom waxes, made by air-blowing of the heated wax, are widely used in polish compositions as extenders for more expensive Carnauba wax.

The relative size of plate, needle, and microcrystals has been found quite constant in studies of many waxes from different sources. This relationship has been discussed previously by Warth (*8*).

## SOLVENT-FRACTIONATION STUDIES

Two solvent-fractionation procedures have been developed and used in studying melting-point distribu-

*Fig. 6. Hexane-acetone method equipment assembly*

tion of the components in petroleum waxes. One procedure is based upon use of mixed hexane-acetone and can be used for all petroleum waxes. The second method, using hexane alone, is unsatisfactory for par-

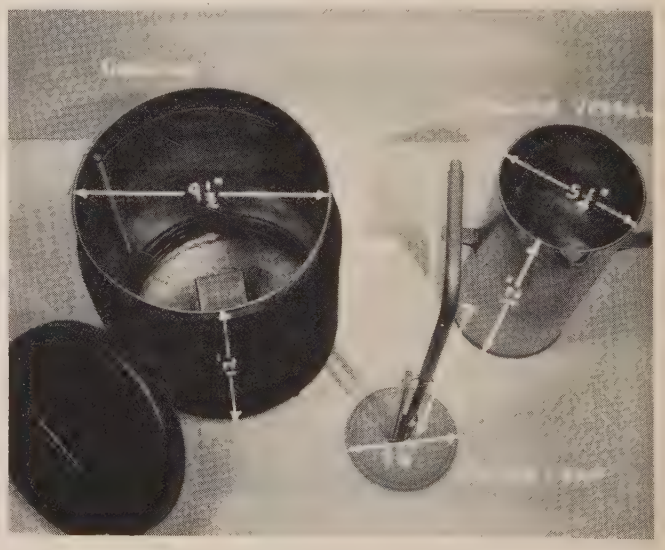

*Fig. 7. Hexane-acetone method cooling and filtering units*

affin waxes but is excellent for residual waxes and blends of residual waxes with polymers, resins, or other materials. In the hexane-acetone procedure, fractions are obtained in sequence from the lowest melting to the highest melting; in the hexane method, the reverse order is followed.

### *Hexane-Acetone Method*

In the hexane-acetone fractionation procedure, crystallization and separation of successive fractions from a 100-gram sample of wax under test are accomplished in a stepwise manner as shown schematically in Fig. 5. Each crystallization step is accomplished by solution of the wax upon heating in 10 to 15 volumes of a 50–50 hexane-acetone mixture, followed by chilling.

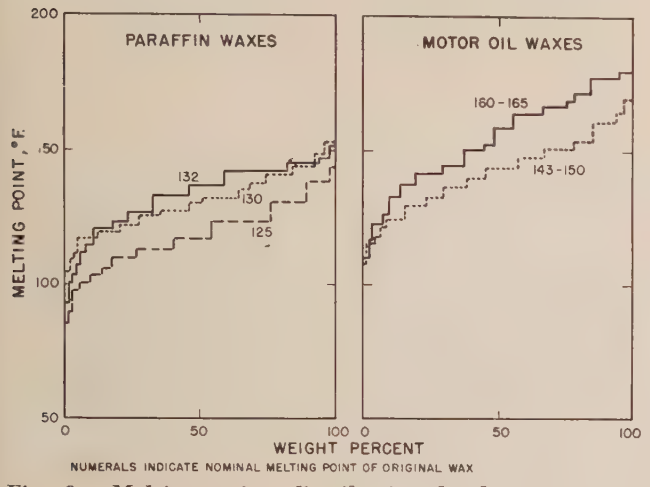


*Fig. 8. Melting point distribution by hexane-acetone method*

Crystallization is started at −60°F., and removal of the solvent by suction separates the fraction soluble at this temperature. Each succeeding step is accomplished by solution of the crystal mass in more solvent, followed by chilling to a temperature 5°F. higher than the preceding fractionation step. The apparatus used for this procedure, shown in Figs. 6 and 7, consists of a cooling bath, a cooling vessel, and a canvas filter leaf used for both agitation and suction. The wax

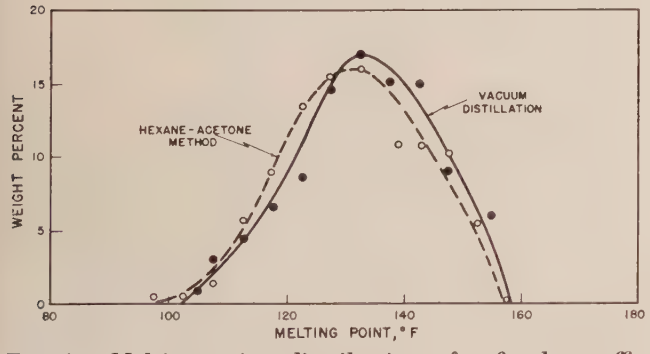


*Fig. 9. Melting point distribution of refined paraffin waxes*

fraction is separated by removal of the solvent in the glass distillation equipment. Additional warm solvent is used in transferring the recovered fraction to a tared beaker for final evaporation and weighing.

*Paraffin Waxes.* Fractionation data obtained by the hexane-acetone procedure on three grades of commercial refined paraffin wax are shown in Fig. 8. These data indicate the width of cut of these waxes and the steady rise in level of melting-point distribution with increase in melting point of the wax. Comparison of data on a refined paraffin wax obtained by solvent fractionation and by vacuum distillation at 1 mm. are shown in Fig. 9. The hexane-acetone procedure yields a melting-point distribution approximating data obtained by the more time-consuming fractional-distillation method. Data on melting-point distribution by calculations from a cooling curve (*9*) were found to be at wide variance with the data in Fig. 9 by both methods.

*Motor-Oil Waxes.* Fractionations of two typical motor-oil waxes by the hexane-acetone procedure yielded the melting-point distributions shown in Fig. 8.

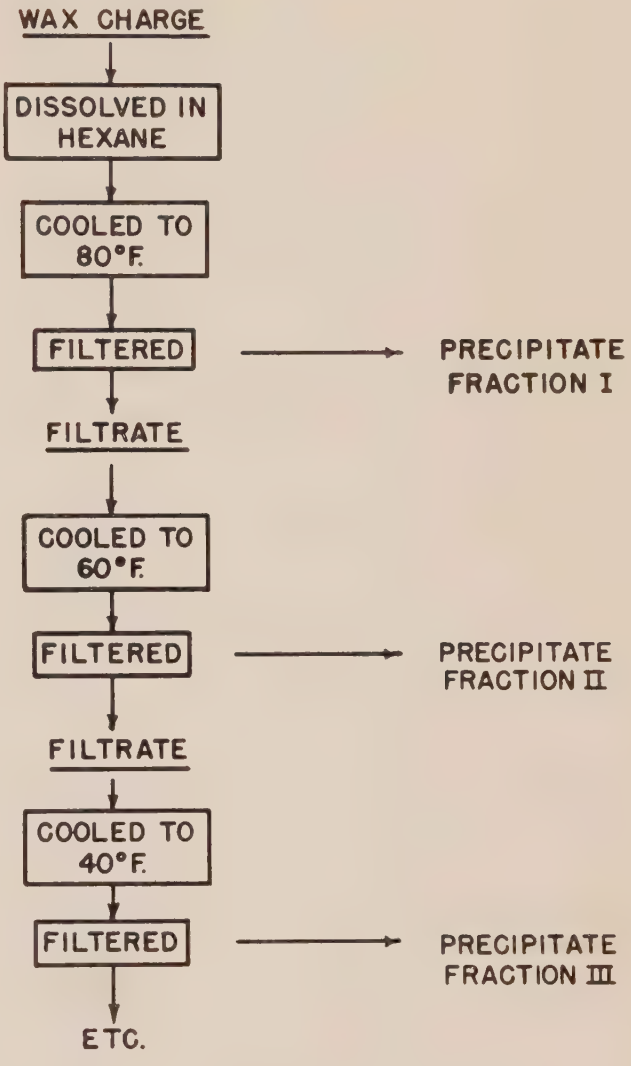


*Fig. 10. Hexane wax fractionation procedure*

These motor-oil waxes show relatively low-oil content with a broad distribution range of crystalline hydrocarbon compounds which are mostly above the range of those in paraffin waxes.

### *Hexane Method*

The hexane fractionation procedure is based upon stepwise crystallization and involves solution of a 60-gram sample of wax in 1500 ml. of hexane followed by successive reduction in temperature from 100°F. to −40°F. in 20° intervals as shown schematically in Fig. 10. A crystalline fraction is removed at each

temperature level by simple gravity filtration through folded filter paper without the use of washing or suction to remove solvent. This provides a series of successively lower-melting fractions which serve to characterize the wax, and which may be further separated by the same procedure to yield a more precise melting-point distribution. These small fractions are usually recombined for simplification of subsequent physical tests. The fractions are generally examined for melting point, flexibility, penetration, viscosity, and crystal form.

This method yields as the final lowest-melting fraction the "oil" cut, which contains oil, low-melting crystalline materials, and any resins or soluble polymers (such as polyisobutylene) that may have been incorporated. Wax compositions containing such relatively insoluble polymers as polyethylene show a separation of these materials at temperatures above that of the first fraction.

*Microcrystalline Waxes.* Typical of the many microcrystalline waxes subjected to the hexane fractionation procedure are five commercial products: Wax A, which is brittle and not suitable for laminating use; two excellent flexible laminating waxes, B and C; and modified waxes D and E, which contain added resins or polymers. Figure 11 shows once-through fractionation data on these five waxes. Brittle wax A shows the absence of the low-melting crystalline fractions present in laminating waxes B and C. The modified waxes are similar to the all-petroleum waxes except for the presence of resinous or polymeric material in the lowest-melting or "oil" fraction.

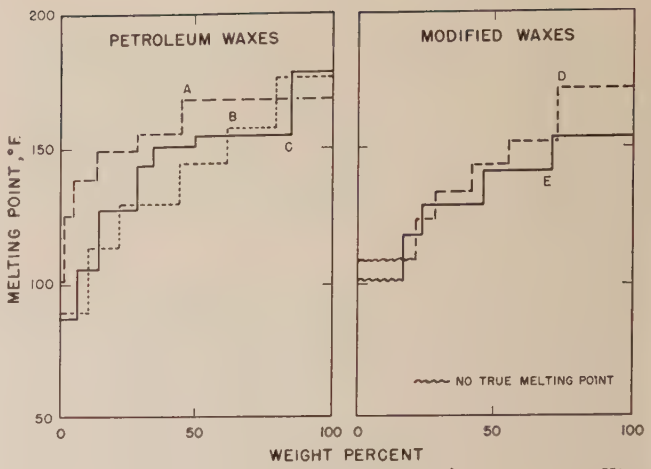


*Fig. 11. Melting point distribution of microcrystalline waxes by hexane method*

**Table II. Properties of Fractions of Microcrystalline Waxes**

| *Fraction no.* | *Brittle point, °F.* | *Penetration, mm./10 at 77°F.* | *Viscosity SSU at 210°F.* |
|---|---|---|---|
| | Petroleum Wax A | | |
| [a] | 80 | 14 | 62.2 |
| 2 | 15 | 41 | 59.6 |
| 3 | 35 | 30 | 55.9 |
| 4 | 45 | 26 | 60.6 |
| 5 | 70 | 23 | 60.3 |
| 6 | 80 | 21 | 61.4 |
| | Laminating Wax B | | |
| [a] | − 5 | 48 | 75.1 |
| 2 | −50 | 360+ | 79.0 |
| 3 | −15 | 53 | 72.2 |
| 4 | 25 | 27 | 72.0 |
| 5 | 32 | 25 | 65.3 |
| 6 | 50 | 18 | 67.4 |
| 7 | 80 | 13 | 79.0 |
| | Laminating Wax C | | |
| [a] | + 5 | 36 | 67.4 |
| 2 | −40 | 360+ | 60.7 |
| 3 | −20 | 60 | 59.4 |
| 4 | −15 | 63 | 57.5 |
| 5 | 0 | 63 | 53.9 |
| 6 | 10 | 32 | 58.1 |
| 7 | 25 | 39 | 59.3 |
| 8 | 50 | 14 | 69.8 |
| 9 | 80 | 11 | 87.9 |
| | Modified Wax D | | |
| [a] | | 36 | 4275 |
| 1 | | (Too soft) | 50,000[b] |
| 2 | | 36 | 188.3 |
| 3 | | 24 | 128.0 |
| 4 | | 19 | 146.9 |
| 5 | | 14 | 99.1 |
| 7 | | 10 | 107.7 |
| | Modified Wax E | | |
| [a] | .. | .. | 90.3 |
| 1 | 15 | (Too soft) | 498 |
| 2 | 10 | 61 | 146.9 |
| 3 | 15 | 35 | 103.1 |
| 4 | 35 | 28 | 86.8 |
| 5 | 35 | 22 | 80.4 |
| 6 | 35 | 18 | 81.1 |
| 7 | 35 | 19 | 80.6 |

[a] Properties of wax before fractionation.
[b] Estimated

Data on melting-point distribution of these five waxes, after refractionation and recombination of the closely melting fractions, are given in Fig. 12 and Table II. The low-melting soft crystalline fractions, which are flexible at very low temperatures, exert a "solubilizing" or crystal-modifying effect on the harder and more brittle higher-melting components. This is the main reason for the difference in service behavior between the brittle wax A and the laminating waxes B and C. Stewart and Nelson (*10*) have shown the beneficial effect of oil on wax plasticity or flexibility, but the addition of more oil to a brittle wax, such as wax A, does not increase the plasticity or flexibility to the degree exhibited by waxes B and C.

The polymeric material obtained from modified wax D was totally unlike oil obtained from petroleum waxes. This material appeared to be of the polyisobutylene type; because of its extremely high viscosity, no effort was made to separate from it any possible resinous material.

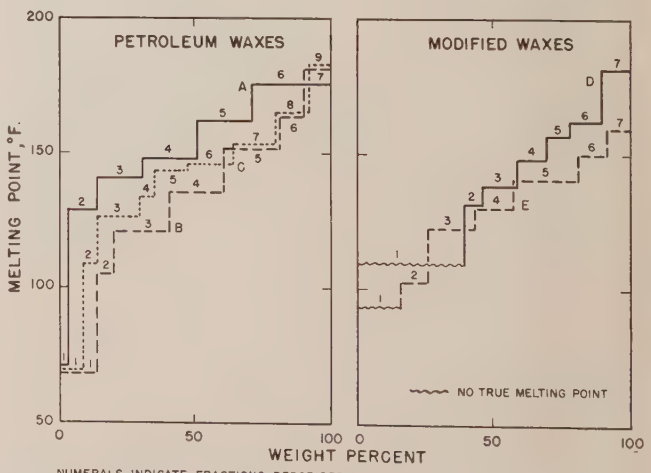


*Fig. 12. Melting point distribution: Refractionation of microcrystalline waxes in hexane*

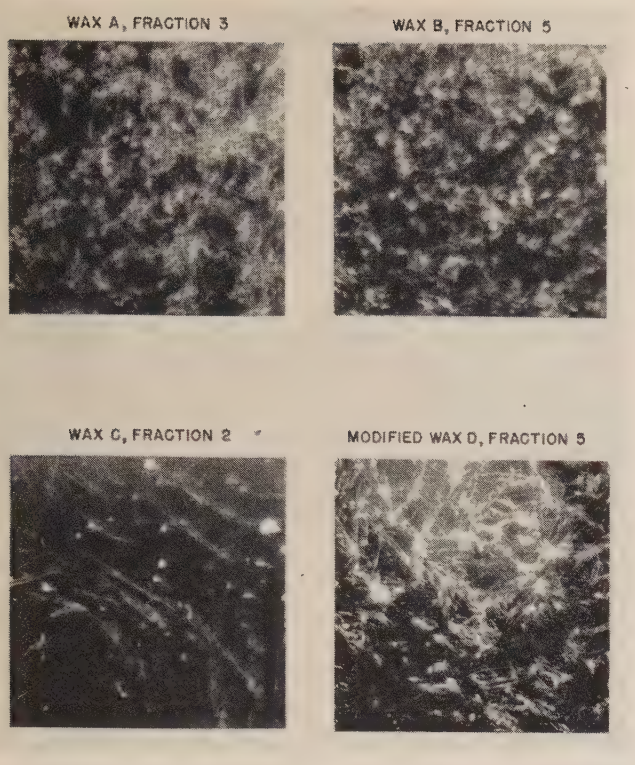


*Fig. 13. Typical crystal forms of microcrystalline wax fractions (200 ×)*

All fractions obtained from these analyses were examined by dark-field microscopy. All crystallizable fractions showed crystal forms typical of microcrystalline waxes as shown in Fig. 13. The "oil" fraction from the unmodified petroleum microcrystalline waxes was not entirely free of wax components as indicated by pour points of 60 to 90°F. Refractionation of these fractions by various solvent techniques yielded oil of low pour point and a small amount of very soft microcrystalline fractions with a melting point of 85 to 95°F.

No materials were found in commercial microcrystalline waxes that might be classified as resins (such as coumarone-indene). In an effort to isolate any possible resinous materials, a dilute hexane solution of the total "oil" fraction from modified wax A was "soaked" with a gross amount of activated Attapulgus clay at 150°F. for 18 hours. The clay was then successively washed thoroughly with hexane, carbon tetrachloride, benzol, and acetone. A light-colored petroleum oil was removed by the hexane; the other solvents yielded only dark petroleum oil such as is obtained by the same procedure from motor oils. Accordingly, the resin content of petroleum microcrystalline waxes must be negligible.

Processing of the "oil" fraction from modified wax E through clay in the same manner yielded a gel-like hexane-soluble polymer fraction and a dark-colored sticky resinous material totally unlike the dark oils isolated from petroleum microcrystalline waxes. The differences in composition between petroleum microcrystalline waxes and modified materials are shown in Fig. 14.

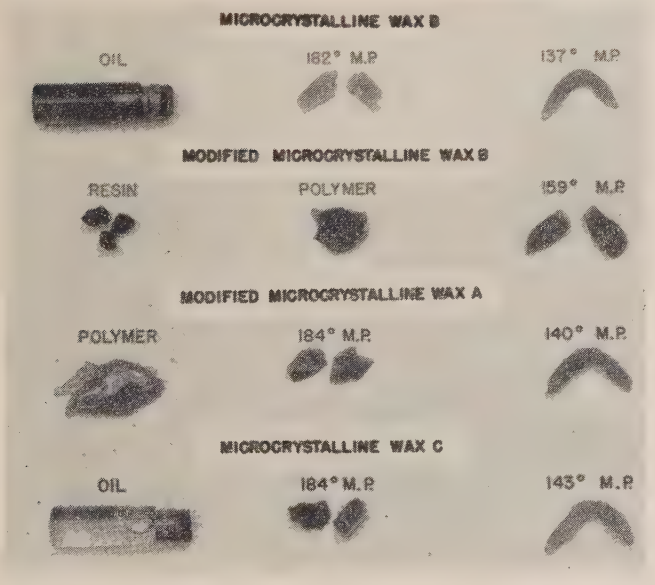


*Fig. 14. Components of commercial laminating waxes*

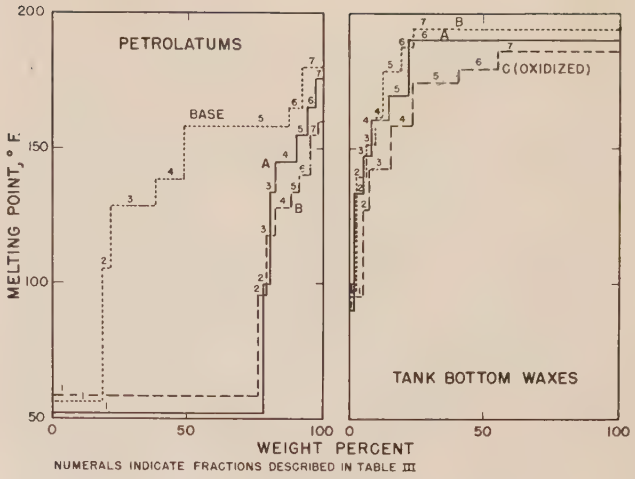


*Fig. 15. Melting point distribution by hexane method*

*Petrolatums.* Fractionation data obtained on two typical petrolatums by the hexane procedure, compared in Fig. 15 with data on a mid-continent petrolatum base (microcrystalline wax), show large amounts of oil and little wax. Properties of the fractions are shown in Table III. Use of this procedure combined with addi-

**Table III. Properties of Petrolatum Fractions**

| *Fraction* | *Penetration, mm./10 at 77°F.* | *Brittle point, °F.* |
|---|---|---|
| | Petrolatum A | |
| 1[a] | (Too soft) | Below −40 |
| 2 | (Too soft) | Below −40 |
| 3 | 63 | −35 |
| 4 | 62 | −30 |
| 5 | 50 | −25 |
| 6 | 33 | 0 |
| 7 | 15 | +80 |
| | Petrolatum B | |
| 1[b] | (Too soft) | Below −40 |
| 2 | (Too soft) | Below −40 |
| 3 | 67 | −30 |
| 4 | 51 | −15 |
| 5 | 41 | −10 |
| 6 | 41 | −10 |
| 7 | 28 | +10 |
| 8 | 26 | +30 |

[a] Viscosity at 210°F. = 48.5 SSU.
[b] Viscosity at 210°F. = 57.5 SSU.

tional laboratory appraisal of the fractions has been of value in correlating the physical behavior of the wax-oil system with composition as shown by melting-point distribution.

*Tank-Bottom Waxes.* Melting-point distributions obtained by the hexane procedure for two typical commercial tank-bottom waxes and an oxidized tank-bottom wax are shown in Fig. 15. The remarkably high percentage of high-melting crystalline material in the tank-bottom waxes is evident. All fractions of oxidized tank-bottom wax contain acidic and saponifiable material but are nevertheless hard, crystalline, and properly classified as waxes. There is only a slight increase in the oil fraction because of oxidation.

## CONCLUSION

The described solvent fractionation procedures provide melting-point distribution data which are of value in characterization of waxes. Petroleum waxes from deasphalted, deresined, and/or acid-treated oil stocks are essentially free of material which might be classed as "resinous colloidal" substances. Resins or polymers which are present in modified products made with petroleum waxes can be isolated through these fractionation procedures.

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Received July 23, 1951. Presented at the Annual Meeting of the Technical Association of the Pulp and Paper Industry, New York, N. Y., Feb. 19–22, 1951.

The assistance of L. P. Schwartz and E. M. B. Pramuk in obtaining these data is appreciated.


# The Reaction of Wood with Alkaline Solutions of Sodium Hydrosulphite


JULIO MONTANO and RALPH HOSSFELD



**By way of extending the study of the action of alkaline reducing agents on wood, aspen sawdust has been treated with aqueous solutions of mixtures of sodium hydroxide and sodium hydrosulphite at 160°C. for a period of 2 hours. The residual wood has been analyzed, and the black liquor investigated for its lignin content and other extractable materials. The residual wood, although greatly reduced in lignin content, was found to be unpulped, the yield increasing with increasing concentration of sodium hydrosulphite in the cooking liquor. Concurrently, the holocellulose content of the residual wood decreased although the per cent recovery of holocellulose increased. Both the lignin and pentosan analyses on the residual wood from cooks to which hydrosulphite had been added were unaccountably erratic. The yield of lignin isolated from the black liquor decreased with increasing concentration of sodium hydrosulphite in the cooking liquor, and at the same time an increasingly large amount of lignin disappeared from the material balance. Analyses of the purified and of the methylated lignins recovered from the black liquors indicated only a slight difference between those obtained from the hydrosulphite cooks and the control made with only sodium hydroxide in the cooking liquor, the former being slightly lower in methoxyl content. The similarity between the results of this study and those reported by others for the cooking of wood with sodium sulphite is discussed. The stability of sodium hydrosulphite under the conditions of these cooks was investigated from which it was found that the material decomposed early in the heating period to give largely sodium sulphite and a small proportion of other unidentified reducing agents.**



Julio Montano, Student, University of Minnesota, and Ralph Hossfeld, Member of TAPPI, Associate Professor of Wood Chemistry, School of Forestry, University of Minnesota, St. Paul, Minn.


The late Dr. Gortner and his students have reported studies of the effect of NaOH (*1*), $Na_2S$ (*3*), $Na_2CO_3$ (*4*), $Na_2S_2O_3$ (*5*), $Na_2SO_4$ (*6*), and NaSH (*17*) on wood under conditions generally associated with the wood pulping processes. Each of these reagents appears to have a particular effect on the constituents of wood: those of alkaline reaction appear to have a pronounced effect on the lignin, while those of acid or neutral reaction appear to have a pronounced effect on the carbohydrate portion of wood. It is of further interest to note that, in these reports and others, a material balance has shown that, in general, only a fraction of the lignin originally present in the wood was isolated from the reaction products. Hagglund (*15*) accounts for the apparent loss by pointing out the presence (*16*) of what he calls a "water-soluble lignin." Aronovsky (*3*) noted a marked disappearance of lignin on treatment of wood with $Na_2SO_3$ and attributed this loss to a depolymerization which rendered the material soluble in the 72% sulphuric acid employed in the determination of lignin. Hossfeld (*17*) noted a similar disappearance of lignin from the material balance when treating aspen wood with aqueous solutions of NaSH and proposed that the reducing nature of this alkaline reagent prevented or inhibited the repolymerization of the hydrolyzed protolignin to the amorphous product which is normally isolated on acidification of the black liquor. It was further proposed that for the same reason it was possible to extract from the acidified black liquor relatively high yields of ether-soluble oils which were taken to represent in part stabilized low molecular weight hydrolysis prod-

ucts from the protolignin originally present in the wood. Later, Brink (*11*) in a study of the ether-soluble oils from NaSH cooks reported the isolation and identification of acetovanillone, *o*-cresol, phenol, 2,6-dimethoxy phenol, and pyrocatechol. Enkvist (*13*) has also reported the isolation of acetovanillone from a similar reaction product, thus further illustrating the possible association of the ether-extractable oils with the ligneous component of the wood.

Another striking feature of the reaction of NaSH with aspen wood was the observation that although the residual wood was greatly reduced in lignin content, the material was completely unpulped (*12*, *17*). Since the unusual nature of the results from attempting to pulp wood with NaSH was attributed to the presence of an alkaline reducing agent, it would be desirable to treat wood under similar conditions with other alkaline reducing agents in order to determine whether similar results are obtained. The present paper is the result of such a study of the action of alkaline solutions of sodium hydrosulphite at 160°C. on aspen sawdust.

## EXPERIMENTAL METHOD

One hundred-gram samples of extractive-free (*20*) aspen sawdust were heated 2 hours at 160°C. in a gas-fired stainless-steel autoclave with 1 liter of liquor containing 25 grams of sodium hydroxide with varying amounts (0, 10, 20, and 30 grams, respectively) of sodium hydrosulphite.

On completion of a cook the residual wood was filtered, washed with distilled water, air-dried, weighed, and set aside for analysis. Analyses of the original and of the residual wood were made according to the methods of the Forest Products Laboratory (*9*) except for the determination of pentosan and methoxyl. The former was made according to the method of Bailey (*7*) using thiobarbituric acid, and the latter according to TAPPI Standard T 2 m-43 (*20*).

The combined black liquor and washings were neutralized to pH 4.0 to 4.5 with HCl and the resulting precipitate filtered, washed, and dialyzed in Visking* bags against distilled water. The filtrate was later exhaustively extracted with *n*-butanol. The dialyzed precipitate was finally recovered by perstillation from the cellophane bags and dried in a vacuum desiccator. The crude product so obtained was further purified (*10*) by repeated precipitation of a methanol solution of the material into excess of dry ethyl ether. The final product from the purification was then washed thoroughly with ethyl ether followed by petroleum ether, and dried in a vacuum desiccator containing paraffin shavings.

Methylation of the purified lignins was carried out according to the methods of Brauns (*10*) first repeatedly with diazomethane (*14*) followed by repeated treatment with dimethyl sulphate. The product from each of the successive treatments with the alkylating agent was purified by the method indicated above before retreatment with the alkylating agent. Acetylation of the purified lignin was carried out also by the method of Brauns using pyridine-acetic anhydride, the final product again being purified by the above method.

**Table I. Yields and Analysis of Products**

| *Liquor composition* | | *Residual wood* | | | | | | *Black liquor* | | | *Methoxyl anal. purified lignin* | | | | *Product recovery* | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | *Crude lignin* | | | *Methylated* | | | | | |
| NaOH, g./l. | $Na_2S_2O_4$, g./l. | Yield, %[b] | Holocellulose, %[a] | Lignin, %[a] | Alcohol-benzene solubility, %[a] | $OCH_3$, %[a] | Pentosan[a] | Yield, %[b] | $OCH_3$, %[a] | Butanol extract, %[b] | Original, %[a] | $CH_2N_2$, %[a] | $Me_2SO_4$ after $CH_2N_2$, %[a] | Acetylated, %[a] | Holocellulose, %[c] | Lignin, %[c] |
| 25 | 0 | 60.1 | 93.55 | 4.34 | 1.48 | 1.21 | 4.49 | 9.74 | 21.54 | 10.0 | 21.37 | 29.10 | 32.8 | 16.90 | 69.8 | 75.4 |
| 25 | 10 | 60.1 | 91.90 | 3.35 | 1.73 | 1.29 | .. | 5.94 | 21.25 | 11.3 | .. | .. | .. | .. | 68.6 | 47.7 |
| 25 | 20 | 62.5 | 91.65 | 5.14 | 1.94 | 1.48 | .. | 3.78 | 21.07 | 13.8 | .. | .. | .. | .. | 71.3 | 42.7 |
| 25 | 30 | 65.4 | 90.95 | 4.68 | 2.17 | 1.51 | 5.46 | 3.20 | 20.96 | 13.9 | 20.35 | 27.60 | 29.55 | 16.73 | 74.0 | 38.3 |
| Original wood | | | 80.45 | 16.38 | 1.57 | 5.0 | 4.35 | | | | | | | | | |

[a] Based on material analyzed.
[b] Based on original oven-dry wood.
[c] Based on constituent present by analysis in original oven-dry wood.

Sodium hydrosulphite is a well-known and widely used reducing agent. Recently it has been studied (*19*) as a bleaching agent for wood pulps but there is, to the writers' knowledge, no report in the literature of studies of the reaction of this reagent with wood at elevated temperatures. Besser, Smith, and Montonna (*8*) have reported the use of alkaline solutions of sodium hydrosulphite at elevated temperature as a chemical retting agent in the processing of flax roving and have recommended this reagent for the isolation of carbohydrate from plant materials in general.

Although the compound $Na_2S_2O_4$ is commonly called sodium hydrosulphite, it is more properly named sodium hyposulphite (*18*) since it is a salt of hyposulphurous acid. The compound appears to be reasonably stable in dilute aqueous alkaline solution. However, at elevated temperatures, aqueous solutions of the salt decompose according to the equation:

$$3Na_2S_2O_4 \rightarrow 2Na_2S_2O_3 + 2NaHSO_3$$

There appears to be no information on the stability of sodium hydrosulphite in alkaline solution at elevated temperatures. On standing in moist air, the compound decomposes ultimately to $Na_2SO_3$ and $SO_2$.

## RESULTS

In discussing the data summarized in Table I it should first be pointed out that those experiments in which

* Cellophane sausage casing manufactured by the Visking Corp., Chicago, Ill.

sodium hydrosulphite was added to the cooking liquor did not yield a cellulosic residue which was pulped in the usual sense of the term. Although the residual material was somewhat lighter in color than the control, there was not the usual softening and disintegration with separation of the fibers. When dry, the residual material was harsh and friable and retained essentially the form of the original wood.†

The yield of residual wood increased with increasing concentration of sodium hydrosulphite in the cook liquor. Concurrently, the holocellulose content of the residue decreased although a material balance indicated a net gain in recovered holocellulose. The alcohol-benzene solubility and methoxyl content of the residual wood were observed to decrease with increasing concentration of sodium hydrosulphite. Lignin and pentosan values on the residual wood were unaccountably erratic. It was noted in attempts to determine pentosan on the residual wood from cook to which hydrosulphite had been added that the furfural distillate developed a deep red color on addition of thiobarbituric acid, the color being presumably due to the presence of excessive amounts of hydroxymethyl furfural. This observation may be of significance with respect to possible alteration of carbohydrate material which in turn might have influenced the lignin determinations in those cooks to which sodium hydrosulphite had been added.

The lignin isolated from those cooks to which sodium hydrosulphite had been added differed in outward appearance from that of the control in that it was at first lighter in color turning to brilliant red on standing. Subsequent purification gave an almost white product which was reasonably stable to discoloration on standing. A qualitative sulphur test on the purified products was negative in each case. The data of Table I show a decrease in yield of lignin as well as an increasing loss from the material balance with increasing addition of sodium hydrosulphite to the cooking liquor.

It was originally anticipated that the disappearance of lignin from the material balance might partially be accounted for by the isolation of relatively larger amounts of solvent-extractable material from the residual acidified black liquor. It was found, however, that in the extreme case there was only a 4% increase in extractive as compared with 37% loss of lignin based on the original wood.

It would appear, then, that the addition of sodium hydrosulphite to the original alkali cooking liquor inhibited the solution of carbohydrate material during the cooking process and that concurrently abnormal amounts of lignin were lost from the material balance. These facts, coupled with the observation that the residual wood from cooks to which hydrosulphite was added was pulped to a much lower degree than the control, bring to attention the strikingly similar results of Aronovsky from his treatment of aspen wood with aqueous solutions of sodium sulphite under similar conditions of reaction time and temperature.

Since sodium hydrosulphite is known to decompose under certain conditions to a mixture of sodium hydrogen sulphite and sodium thiosulphate, blank cooks were made in which the original cook liquor was heated along at 160°C. for as little as 15 minutes. In all cases the sodium hydrosulphite was found to have completely decomposed to give large amounts of sodium sulphite, along with small amounts of unidentified reducing agent (*20*).

It may well be inferred, therefore, that the results of these experiments have not been due to the presence of sodium hydrosulphite in the cooking liquor but rather to the combination sodium sulphite with sodium hydroxide. However, one cannot overlook the possible effect of the original hydrosulphite on the wood in the short period before decomposition of the reagent has been affected.

The results of methylation and acetylation of the isolated and purified lignins are summarized in Table I from which it may be seen that the lignin from the cook to which 30 grams per liter sodium hydrosulphite had been added did not appear to differ greatly from the control. Although there appears to be slightly decreased methoxyl in the former, the principal point of difference appears to be in the previously mentioned color of the products, and in the comparative solubility of the two products in the common lignin solvents. The products from the hydrosulphite cooks were slightly less soluble in dry dioxane, and the recovery from solvent purification of the crude material was 34.8% compared to 15.0% in the case of the lignin from the control.

† It was later learned through a personal communication from F. Smith of the Division of Agricultural Biochemistry of the University of Minnesota, that aspen chips, in contrast with sawdust, were more satisfactorily pulped. It is suggested that differences in rate of penetration of the liquor constituents may be responsible for the differences in pulping action.

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Received Feb. 20, 1951.

From a thesis by Julio Montano presented to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the M.S. degree, January, 1950. Paper No. 2272 in the Scientific Journal Series of the Minnesota Agricultural Experiment Station, St. Paul, Minn.

The authors wish to acknowledge the cooperation of Fred Smith of the Division of Agricultural Biochemistry of the University of Minnesota in initiating this study.

# Formation of Sodium *p*-Azobenzenesulfonate from Nitrobenzene and Kraft Black Liquor

WILLIAM R. CSELLAK

The formation of sodium *p*-azobenzenesulphonate (SPABS) as a reduction product from the action of sulphite waste liquor and alkali on nitrobenzene was reported by Pearl (*1*). Another paper by Pearl (*2*) described the identification of this salt and some of its reactions. Pearl (*2*) also proved that the formation of SPABS must result from the reduction of nitrobenzene by lignin in an alkaline solution with the subsequent sulphonation of the reduced product in an active state by inorganic sulphites.

In another article (*3*) by the author it was reported that SPABS may also be obtained as a reduction product from the action of kraft black liquor on nitrobenzene. The present paper describes a quantitative method for the estimation of SPABS and, in addition, indicates that the two reducing agents in kraft black liquor (sodium sulphide and sodium thiosulphate) are mainly responsible for the formation of SPABS in the above reaction.

Contrary to the reducing action of sulphite waste liquor, the SPABS from the kraft black liquor oxidations was formed only under superatmospheric conditions (140–200°C.), and separated from the reaction mixture as orange-colored platelets. Since SPABS was not formed in an oxidation in which an isolated kraft lignin (Indulin A) was substituted for the kraft black liquor, a study was undertaken to determine whether the inorganic constituents of kraft black liquor alone will bring about the formation of SPABS. The oxidations in this study were patterned after the kraft black liquor oxidation which gave the highest yield of SPABS and were simulated with a hypothetical black liquor containing only the inorganic constituents. Based on 222 grams of water, Table I lists the amounts of salts which were used in addition to the sodium hydroxide and nitrobenzene. These figures correspond generally to the maximum amounts found in kraft black liquor as reported by Sutermeister (*4*).

The results of this study are summarized in Table II. Experiment 3, made with all the inorganic constituents, gave a yield (17.1 grams) of SPABS greater than that obtained using kraft black liquor (experiment 1). This was probably due to the fact that the above amounts of inorganic salts exceeded the amounts present in the black liquor used. Experiment 2 showed that SPABS is not formed in the absence of the inorganic constituents. Experiment 4 showed that the presence of sodium sulphite was not required for the sulphonation of the SPABS. Experiment 5 proves that sodium sulphide is primarily responsible for the formation of SPABS and that the reaction is accomplished by a simultaneous reduction and sulphonation of the nitrobenzene. In this experiment the sodium sulphide was quantitatively transformed to SPABS. Experiments 6 and 7 show the effect of the other salts in the reaction, particularly the effect of the sodium thiosulphate.

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**Table I. Inorganic Salts Used in Simulated Black Liquor**

| | *Grams* |
|---|---|
| Sodium carbonate | 5.6 |
| Sodium sulphide | 4.0 |
| Sodium sulphate | 2.7 |
| Sodium thiosulphate | 1.4 |
| Sodium sulphite | 1.4 |

In order to facilitate the separation and identification of SPABS by comparison with authentic SPABS, a benzylthiuronium derivative (*5*) was prepared. The quantitative nature of this reaction and the relative insolubility of the derivative were indicated by the yield of 99.6%. Since SPABS has no melting point and, consequently, its purity and yield are difficult to determine, the preparation of the above derivative in practically quantitative yields serves as a rapid method for analysis of SPABS in mixtures free of materials which react with the reagent.

## EXPERIMENTAL

The kraft black liquor was a product (Thilmany Pulp & Paper Co.) from the commercial kraft pulping of jack pine. The black liquor had a solids content of 21.85% and the solids contained 4.17% methoxyl.

The Indulin A was an isolated kraft lignin prepared by the West Virginia Pulp and Paper Co.

The reduction was accomplished in a Parr hydrogenation apparatus autoclave of approximately 400-ml. capacity. The autoclave was charged with 284 grams of kraft black liquor, 42 grams of sodium hydroxide, and 63 grams of nitrobenzene. The contents were heated to 170°C. in 45 minutes and maintained at that temperature for 3 hours. Upon cooling, the contents were emptied and the golden-orange platelets of SPABS were filtered, washed with a small amount of water, dried, and weighed.

The experiments listed in Table II were performed in essentially the same manner. In addition to the materials listed, the reaction mixture consisted of 222 grams

**Table II. Formation of SPABS from Nitrobenzene**

| *Expt.* | *Reaction Mixture*[a] | *SPABS, g.* |
|---|---|---|
| 1 | Kraft black liquor | 15.1 |
| 2 | Indulin A | 0 |
| 3 | $Na_2S$, $Na_2SO_4$, $Na_2S_2O_3$, $Na_2SO_3$ | 17.1 |
| 4 | $Na_2S$, $Na_2SO_4$, $Na_2S_2O_3$ | 17.6 |
| 5 | $Na_2S$ | 15.8 |
| 6 | $Na_2SO_4$, $Na_2S_2O_3$, $Na_2SO_3$ | 7.2 |
| 7 | $Na_2SO_4$, $Na_2SO_3$ | 3.3 |

[a] In addition to water, NaOH, and nitrobenzene.

of water, 42 grams of sodium hydroxide, and 63 grams of nitrobenzene. In experiment 2, 17.8 grams of Indulin were used.

The material upon recrystallization from alcohol was obtained as iridescent orange platelets.

*Analysis.* Calculated for $C_{12}H_9N_2NaO_3S$: N, 9.86; S, 11.27; Na, 8.10. Found: N, 9.77; S, 10.80; Na, 8.18.

***Preparation of Benzylthiuronium Derivative***

To a solution of 1.75 grams of SPABS in 300 ml. of warm water (60°C.) was added a concentrated aqueous solution of 2.50 grams of benzyl isothiourea hydrochloride with stirring. An immediate precipitate of shiny orange platelets, somewhat lighter in color than the original SPABS, was obtained. After chilling, the derivative was filtered, washed with cold water, air dried, and recrystallized to constant melting point from 50% ethanol. The melting point of this new sulphonic acid derivative was 219–220°C. (uncorr.). There was no depression of mixed melting point with the derivative prepared from authentic SPABS (*2*). The yield was 99.6%.

*Analysis.* Calculated for $C_{20}H_{20}N_4O_3S_2$: N, 13.08. Found: N, 13.08.

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Received May 23, 1951. A portion of a thesis submitted in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence College, 1950. This work was carried out under the direction of Irwin A. Pearl.


# The Reaction Between Kraft Black Liquor and Nitrobenzene


WILLIAM R. CSELLAK



**In this study of the oxidation of kraft black liquor with nitrobenzene, the optimum yield of benzene-soluble products was 31.2% based on the lignin. A somewhat similar oxidation made on a larger scale to permit the separation and identification of the above cleavage products gave a yield of 17.6%. Vanillic acid accounted for 10.1% (yield of 1.78% based on lignin), and acetovanillone for 3.8% (0.66% based on lignin) of the fraction. Vanillin and oxlic acid were also isolated and identified. In a similar large-scale oxidation the yield of vanillin was approximately 0.3% (based on lignin) in contrast to the yield of 6.4% (based on lignin) which was obtained in a small-scale oxidation. A procedure which was based on the solubilities of the lead salts in water and dilute ethanol was developed for the fractionation of the bicarbonate-soluble materials into five separate divisions. Crystalline compounds were isolated from four of these fractions by means of sublimation. The data obtained on one of these compounds indicate some similarity of this compound ($C_9H_9O_2$) with cinnamic acid and coumarin. Two unidentified phenolic derivatives were prepared from compounds present in the sodium hydroxide-soluble fraction. The remainder and greater portion of the benzene-soluble materials consisted of oils and amorphous materials which represented either high molecular weight lignin cleavage products or condensation products of the lignin. The nitrobenzene reduction products, which were formed in the large-scale oxidation, consisted of aniline and azobenzene. In addition to these, azobenzene and sodium *p*-azobenzenesulphonate (SPABS) were formed in some of the small-scale oxidations.**


Although numerous investigations have been made on the oxidation of the lignosulphonic acids in sulphite waste liquor [summarized by Pearl (*1*)], very little has been done with the recovery of similar products from the more abundant kraft black liquor. Although Schulz's patent (*2*) on the nitrobenzene oxidation of sulphite waste liquor covers all lingin-containing materials, the only known attempt to oxidize the lignin in kraft black liquor was made by Breneck and Müller (*3*), who obtained 1.2 grams of vanillin by heating 1 liter of kraft black liquor for 30 hours at 103°C. in the presence of a stream of oxygen. Since higher yields of vanillin were obtained by oxidizing sulphite waste liquor with nitrobenzene, the following study was made to determine whether similarly higher yields of vanillin could be obtained by oxidizing kraft black liquor with nitrobenzene and to determine the nature of the other products formed in the reaction.


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### NATURE OF KRAFT BLACK LIQUOR USED

A 55-gallon drum of commercial black liquor used in this study was obtained from the Thilmany Pulp and Paper Co. The conditions under which this black liquor was prepared are listed in Table I.

In order to cover a wider range of variables in the oxidations, a more concentrated black liquor was required. This was prepared by concentrating under reduced pressure (at 35°C.) 5 gallons of the original black liquor to less than half its original volume. This material was slightly sirupy in nature.

The analyses made on the liquor in accordance with TAPPI Standard 625 m-48 are summarized in Table II. Lignin in the black liquor was calculated from the percentage of total solids and the methoxyl in the solids, assuming that all the methoxyl was in the lignin and that the methoxyl content of the lignin was 14.5%.

### STUDY OF OPTIMUM OXIDATION CONDITIONS

The oxidations were carried out in the manner described by Pearl and Lewis (*4*). Kraft black liquor was used instead of sulphite waste liquor, and the reactants were brought to a boil in 45 minutes.

The alkaline reaction mixture was transferred to a continuous extractor in which the unreduced nitrobenzene and its reduction products were extracted with ether. The ether-extracted alkaline solution was acidified to approximately pH 2 by slowly adding sulphuric acid with violent agitation and then filtered or centrifuged. The amber-colored acid filtrate was extracted

**Table I. Conditions Under Which Black Liquor Was Prepared**

| | |
|---|---|
| Date of cook | December 15, 1947 |
| Wood pulped | 8.5 cords of 100% green jack pine |
| Type of digester | Direct heating rotary (1935 cu. ft. capacity) |
| Cooking liquor | |
| Dilute black liquor | 178 gal. |
| White liquor | 3822 gal. (equivalent to 36 lb. active $Na_2O$) |
| TAPPI sulphidity | 25 |
| Maximum pressure | 105 lb. |
| Time to maximum pressure | 92 min. |
| Time at maximum pressure | 90 min. |
| Blowing characteristics | Started to blow at 66-lb. pressure with a total blowing time of 20 min. |
| Permanganate no. of stock | 20.3 (somewhat softer than for standard wrapping grade) |
| Black liquor sample | 55 gal. drawn off directly from the diffuser |

with ether in a continuous extractor; the precipitate was air dried, ground to 40 mesh, and extracted with ether in a Soxhlet extractor. The average extraction was continued for 60 hours.

The ether extracts from the acid filtrate and precipitate were combined, dried with anhydrous sodium sulphate, freed of ether by distillation on a water bath, and weighed.

### *Superatmospheric Pressure Oxidations*

These oxidations were made in a stainless steel autoclave (Parr hydrogenation apparatus) as described by Pearl and Lewis (*4*). Upon completion of the oxidation, the mixture was allowed to cool to 80°C. with rocking, then cooled to room temperature under tap water, and the reaction mixture was removed from the autoclave. The precipitate in the reaction mixture was centrifuged or filtered through a sintered-glass funnel. washed with a small amount of water, and extracted with ether. This ether extract was combined with the ether extract obtained from the continuous extraction of the alkaline filtrate. The reaction mixture was then treated in the same manner as described for the atmospheric pressure oxidations.

**Table II. Black Liquor Analysis**

| | *As received* | *Concentrated* |
|---|---|---|
| Specific gravity | 1.135 | 1.336 |
| Solids, % | 21.85 | 45.6 |
| Methoxyl, % | 4.17 | 4.28 |
| Sulphated ash as NaOH, % | 40.2 | ... |
| Organic matter, % | 59.8 | ... |
| Lignin (calcd.), % | 6.28 | 13.45 |
| Active alkali (as NaOH), g./l. | 26.9 | 56.1 |
| $Na_2S$ (as NaOH), g./l. | 15.8 | 33.0 |
| NaOH (as NaOH), g./l. | 11.1 | 23.1 |
| Total alkali (as NaOH), g./l. | 82.3 | 171.8 |

The experimental conditions and the yields of products from the various oxidations are presented in Table III. The yield data are reported as the percentage yield of benzene-soluble fractions based on lignin* in the black liquor and also as the percentage of methoxyl recovered in the benzene-soluble products.

The yield of benzene-soluble fractions was believed to be the most desirable means of determining the degree of oxidation of the lignin and afforded the best comparison of the various oxidations. Previous investigators in the field of lignin oxidation were mainly interested in high yields of vanillin. However, since this was to be a fundamental study of the reaction between nitrobenzene and kraft black liquor, it was desirable to obtain a high yield of a fraction which contained all the related guaiacol compounds. After obtaining the highest possible yield of benzene-soluble materials, the second part of this study was to determine the exact nature and yields of the individual constituents in the benzene-soluble products.

## EXTRACTION OF BLACK LIQUOR

In order to determine the nature of the ether- and benzene-soluble materials present in the black liquor before oxidation, 9 liters of kraft black liquor, as received, were extracted with ether in a continuous extractor. The ether extract was dried with anhydrous sodium sulphate, and the ether was distilled to give 30.3 grams (3.4

* As defined by method of analysis. A portion of this value actually comprises lignin degradation products.

**Table III. Summary of Small-Scale Oxidations**

| *Oxidation* | *Black liquor, g.* | *Lignin, g.* | *NaOH in black liquor, g.* | *NaOH added, g.* | *$C_6H_5NO_2$, g.* | *Reactant ratio based on 1 part lignin,* $C_6H_5NO_2$ | *NaOH* | $H_2O$ | *Max. temp., °C.* | *Time at max. temp., hr.* | *Benzene solubles* *Yield, g.* | *Yield (based on lignin), %* | *$OCH_3$, %* | *$OCH_3$ recovered, %* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1[a] | 568 | 35.7 | 5.6 | 42.0 | 42.0 | 1.2 | 1.3 | 12.4 | 103 | 8 | 6.91 | 19.4 | 9.70 | 13.0 |
| 3[b] | 443 | 61.2 | 7.7 | 0 | 72.0 | 1.2 | 0.1 | 4.0 | 107 | 8 | 10.69 | 17.4 | 10.9 | 13.2 |
| 4[b] | 443 | 61.2 | 7.7 | 72.0 | 144.0 | 2.4 | 1.3 | 4.0 | 117 | 8 | 13.38 | 21.6 | 11.1 | 16.8 |
| 5[b] | 334 | 46.1 | 5.8 | 0 | 54.2 | 1.2 | 0.1 | 4.0 | 170 | 3 | 5.26 | 11.4 | 8.18 | 6.4 |
| 6 | 284 | 17.8 | 2.8 | 0 | 21.0 | 1.2 | 0.1 | 4.0 | 170 | 3.5 | 3.24 | 18.1 | 11.3 | 14.3 |
| 7 | 284 | 17.8 | 2.8 | 21.0 | 21.0 | 1.2 | 1.3 | 12.4 | 170 | 3 | 4.32 | 24.2 | 10.15 | 17.0 |
| 8 | 284 | 17.8 | 2.8 | 21.0 | 42.0 | 2.4 | 1.3 | 12.4 | 170 | 3 | 5.57 | 31.2 | 12.89 | 27.8 |
| 9 | 284 | 17.8 | 2.8 | 21.0 | 63.0 | 3.6 | 1.3 | 12.4 | 170 | 3 | 6.47 | 36.2 | 10.24 | 25.5 |
| 10 | 284 | 17.8 | 2.8 | 42.0 | 63.0 | 3.6 | 2.5 | 12.4 | 170 | 3 | 5.57 | 31.2 | 11.62 | 25.1 |
| 11 | 284 | 17.8 | 2.8 | 42.0 | 63.0 | 3.6 | 2.5 | 12.4 | 170 | 1 | 5.64 | 31.6 | 10.87 | 23.6 |
| 12 | 284 | 17.8 | 2.8 | 42.0 | 63.0 | 3.6 | 2.5 | 12.4 | 200 | 1 | 4.59 | 25.7 | 9.54 | 17.0 |
| 13 | 227 | 14.3 | 2.2 | 42.0 | 126.0 | 8.8 | 3.1 | 12.4 | 200 | 1 | 4.40 | 30.8 | 7.09 | 15.0 |
| 14 | 284 | 17.8 | 2.8 | 42.0 | 63.0 | 3.6 | 2.5 | 12.4 | 200 | 3 | 2.45 | 13.7 | 9.55 | 8.9 |
| 15 | 227 | 14.3 | 2.2 | 42.0 | 126.0 | 8.8 | 3.1 | 12.4 | 200 | 3 | 1.43 | 10.0 | 4.37 | 2.9 |
| 16 | 227 | 14.3 | 2.2 | 84.0 | 126.0 | 8.8 | 6.0 | 12.4 | 200 | 1 | 2.38 | 16.5 | 2.85 | 3.4 |
| 17 | 227 | 14.3 | 2.2 | 84.0 | 126.0 | 8.8 | 6.0 | 12.4 | 200 | 3 | 2.06 | 14.4 | 2.32 | 2.4 |
| 18[c] | .. | 17.8 | .. | 23.8 | 42.0 | 2.4 | 1.3 | 12.4 | 170 | 3 | 4.11 | 23.0 | 12.07 | 19.3 |
| 19 | 284 | 17.8 | 2.8 | 21.0 | 42.0 | 2.4 | 1.3 | 12.4 | 140 | 6 | 5.01 | 28.1 | 9.66 | 18.5 |
| 20 | 568 | 35.7 | 5.6 | 42.0 | 84.0 | 2.4 | 1.3 | 12.4 | 105 | 8 | 7.41 | 20.8 | 9.49 | 13.6 |
| 21[b] | 334 | 46.1 | 5.8 | 54.2 | 108.4 | 2.4 | 1.3 | 4.0 | 170 | 1 | 9.91 | 21.5 | 8.17 | 12.1 |

[a] Schulz's proportions.
[b] Concentrated black liquor.
[c] Indulin A used instead of black liquor.

grams per liter of black liquor) of an ether-soluble oil with a strong mercaptan odor. When the oil was distilled under reduced pressure, the residue consisted of 8.2 grams (0.9 gram per liter) of a yellow-brown solid; the distillate was a red liquid. The yellow-brown solid was dissolved in a small quantity of ether. A white crystalline material failed to dissolve and was filtered. The crystals, on being freed of ether, changed to an oil. The oil yielded a cream-colored powder, which still had a mercaptan odor, on long standing.

The ether-extracted kraft black liquor was devoid of any odor. However, after several months of standing, a slight kraft odor was again observed. A 500-ml. aliquot of the extracted black liquor was acidified with sulphuric acid to a pH of approximately 2. The brown precipitate was filtered, dried, ground to a fine powder, and extracted with ether in a Soxhlet extractor. The light brown filtrate was extracted with ether in a continuous extractor.

The ether extracts from the precipitate and filtrate were combined and dried with anhydrous sodium sulphate, and the ether was distilled on a water bath. The yield of ether-soluble oil was 12.23 grams. The ether-soluble materials were converted to a benzene-soluble fraction by dissolving the ether-soluble oil in 122 ml. of acetone, filtering a small amount of sulphur, and precipitating the acetone solution dropwise into 2440 ml. of benzene with rapid stirring. The red solution was decanted from the precipitated tar, and the acetone was removed by distillation at constant volume. The acetone-free solution was again decanted and the benzene was distilled under reduced pressure. The yield of benzene-soluble materials was 10.3 grams (28.9% based on the lignin). The methoxyl content was 10.26%. This represents a recovery of 20.5% of the original methoxyl in the black liquor.

### LARGE-SCALE OXIDATION

In order to secure a larger sample of the benzene-soluble material which would permit the identification of products formed in extremely low yields, a large-scale oxidation was made under the conditions giving the best yield among the small scale oxidations (oxidation 8).

This oxidation was made in a stainless steel, cylindrical, horizontal rotary autoclave having a capacity of 33.7 liters. The autoclave was equipped with a relief valve, a safety pressure gage, and a thermometer well. The rate of rotation was 20 revolutions per hour.

The autoclave was charged with 20 liters of kraft black liquor, 1680 grams of sodium hydroxide pellets, and 2780 ml. (3360 grams) of nitrobenzene. The charging hole plug was screwed on and rotation was started. The contents were heated to 170°C. in 45 minutes; this temperature was maintained for 3 hours. Heating was then discontinued and the autoclave and contents were allowed to cool to room temperature while rotating. Contrary to the results obtained in oxidation 8, the reaction mixture had a nitrobenzene odor and did not contain a precipitate. The last traces of the reaction mixture were washed out of the autoclave with a stream of water.

The alkaline reaction mixture and washings (comprising a volume of 27 liters) were filtered and transferred to a large continuous extractor in which the nitrobenzene and its reduction products were removed with benzene. The benzene extract of nitrobenzene and its reduction products comprised a volume of 14 liters.

The benzene-extracted alkaline reaction mixture was acidified to approximately pH 2 by adding concentrated sulphuric acid with rapid stirring. Because of foaming and to avoid a great temperature rise, the acidification was accomplished by periodic additions of sulphuric acid. After 2 days the desired pH was attained.

The acidified mixture was centrifuged in a basket centrifuge. The acid filtrate was extracted to exhaustion with benzene in continuous extractors. Upon completion of the extraction, the benzene was distilled under reduced pressure; 59.7 grams of a brown benzene-soluble oil were obtained.

The precipitate of lignin and sodium sulphate obtained by centrifuging the acidified reaction mixture was air dried and ground in a Wiley mill to pass a 40-mesh screen. The tan powder was extracted with benzene in three large Soxhlet extractors. The benzene extract was distilled under reduced pressure to yield 245.9 grams of a brown benzene-soluble oil. The combined yield from the filtrate and the precipitate was 305.6 grams. The crystals of sulphur which formed in the benzene-soluble fractions were removed by dissolving the oil in ethanol and filtering the sulphur. Upon removing the ethanol by distillation under reduced pressure, a combined yield of benzene-soluble materials of 251.2 grams (17.6% based on the lignin) was obtained. The methoxyl content was 10.8%, which represents a recovery of 13.1% of the original methoxyl content of the black liquor.

The waste benzene-extracted acid filtrate was boiled to remove sulphur dioxide, cooled, and extracted with ether in a continuous extractor. The benzene-extracted lignins were also extracted with ether. A combined yield of 263.5 grams of red-brown, ether-soluble oil was obtained. The methoxyl content was 6.1%.

The benzene- and ether-extracted precipitated lignin had a methoxyl content of 3.2%. An aliquot of the extracted acid filtrate was evaporated to dryness. The methoxyl content of the solids was 0.14%. The methoxyl balance, showing the distribution of the original 206.8 grams of methoxyl in the black liquor, is summarized in Table IV.

The various steps in the class separations of a 101.5-gram aliquot (40.4%) of the benzene-soluble materials are schematically outlined in Fig. 1. In essence, the extractions were made with 21% sodium bisulphite solution, saturated sodium bicarbonate solution, and 5% sodium hydroxide solution. The total yields from the oxidation are summarized in Table V.

*Analysis of Bisulphite-Soluble Fractions.* The bisulphite-soluble oils were distilled under reduced pressure; 3.94 grams of a yellow sirupy material distilled at 65 to 72°C./0.04 mm. while the bath temperature was maintained at 140°C. Raising the bath

**Table IV. Methoxyl Distribution After Oxidation**

| *Fraction* | *Methoxyl, g.* | *Methoxyl, %* | *Percentage of original* |
|---|---|---|---|
| Benzene-soluble | 27.2 | 10.84 | 13.1 |
| Ether-soluble | 16.2 | 6.14 | 7.8 |
| Precipitated lignin | 158.3 | 3.19 | 76.5 |
| Acid filtrate | 4.5 | 0.14[a] | 2.3 |
| Total | 206.2 | ... | 99.7 |

[a] Based on solids.

temperature to 180°C. failed to produce any additional distillate. The yellow sirup consisted of a few crystals, which were identified as sulphur, and a yellow oil. This oil was insoluble in water, petroleum ether, and ligroin. Attempts to obtain a crystalline product from dilute ethanol, ether-petroleum ether, and benzene-ligroin mixtures failed. The oil was soluble in bisulphite but failed to yield crystalline derivatives with phenylhydrazine, hydroxylamine, and 2,4-dinitrophenylhydrazine. Oily derivatives were obtained except with the latter reagent, in which case no reaction was believed to have taken place.

The bisulphite-soluble undistillable materials were taken up in absolute ether for transfer to a sublimation apparatus. The material was only slightly soluble in ether. Hence, the remainder of the material was dissolved in absolute ethanol. When the alcohol solution was combined with the ether solution, a light brown ligninlike precipitate was formed. This was filtered and washed with ether. On drying, the precipitate (8.6 grams) turned into a dark tarry material. The light brown amorphous character was restored on the surface of the tar when the material was resuspended in ether.

The solvent was distilled from the filtrate under reduced pressure. The brown oily product (20 grams) was sublimed in an oil bath (90°C.) under a pressure of 0.04 mm. After a 24-hour sublimation period, 0.4 gram of a white solid (slightly moist with oil) was obtained. A small portion of the solid was placed on a porous plate, briefly washed with ether, and the melting point determined. The white crystals melted at 203°C.,† which was indicative of vanillic acid. The white solid was completely sublimed from the residue after 32 days of continuous heating. During the latter stages of the sublimation, the bath temperature was raised to 100°C.

† All melting points are uncorrected and were determined on a Fisher-Johns melting point apparatus unless otherwise indicated.

**Table V. Composition of Benzene-Soluble Materials**

| *Fraction* | *Yield, g.* | *Methoxyl, %* | *Yield (based on benzene-soluble fractions), %* | *Yield (based on lignin), %* |
|---|---|---|---|---|
| Bisulphite-soluble | 88.0 | 15.7 | 35.1 | 6.2 |
| Bicarbonate-soluble | 56.5 | 8.2 | 22.6 | 4.0 |
| Alkali-soluble | 63.2 | 16.0 | 25.2 | 4.4 |
| Neutral | 3.8 | .. | 1.5 | 0.3 |
| Total | 211.5 | .. | 84.4 | 14.9 |

and then to 120°C. to speed the removal of the solid. The yield of sublimate was 8.8 grams. The vanillic acid in the above sublimate was separated from the oil by extracting with hot water and 8% sodium bicarbonate solution. After repeated extractions, the sublimate was resolved into 1.7 grams of a red-brown oil and 7 grams of vanillic acid. The vanillic acid melted at 207–208°C. (capillary) and did not depress a mixed melting point with authentic vanillic acid.

*Analysis.* Calculated for vanillic acid, $C_8H_8O_4$: $CH_3O$, 18.44%. Found: $CH_3O$, 18.38%.

The oil had a methoxyl content of 17.52% and a sulphur content of 1.45%. Further analysis failed to disclose the nature of this oil.

*Isolation of Vanillin.* In an analogous qualitative large-scale oxidation, in which a portion of the oxidized kraft black liquor was lost during the steam distillation of the acidified reaction mixture, a similar bisulphite-soluble fraction was obtained. However, in this case, the acidified bisulphite extract was boiled under a reflux for several days without completely removing the sulphur dioxide and the mercaptan odor. The acid solution was then saturated with sodium chloride and extracted to exhaustion with ether in a continuous extractor.

The ether-extracted acid solution retained a golden

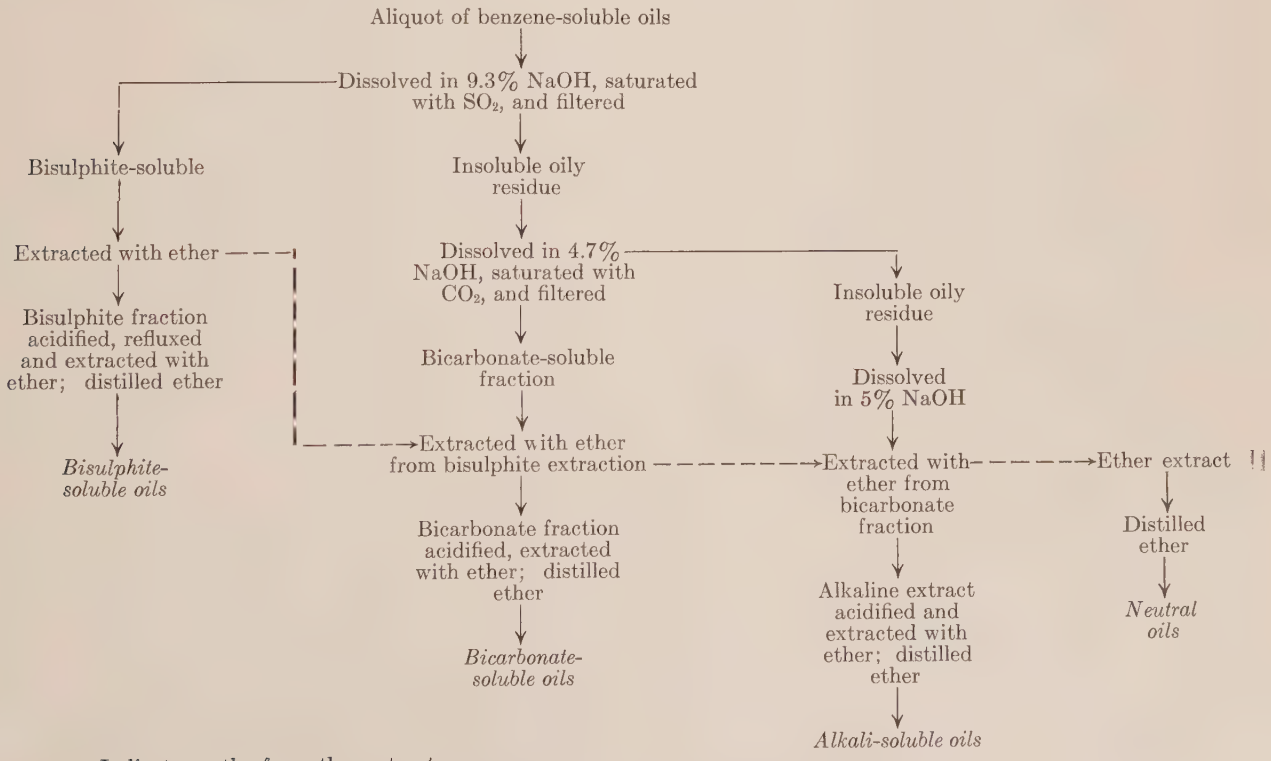
Aliquot of benzene-soluble oils
Dissolved in 9.3% NaOH, saturated with $SO_2$, and filtered
Bisulphite-soluble
Insoluble oily residue
Extracted with ether
Dissolved in 4.7% NaOH, saturated with $CO_2$, and filtered
Insoluble oily residue
Bisulphite fraction acidified, refluxed and extracted with ether; distilled ether
Bicarbonate-soluble fraction
Dissolved in 5% NaOH
Extracted with ether from bisulphite extraction
Extracted with ether from bicarbonate fraction
Ether extract
Bisulphite-soluble oils
Bicarbonate fraction acidified, extracted with ether; distilled ether
Distilled ether
Neutral oils
Bicarbonate-soluble oils
Alkaline extract acidified and extracted with ether; distilled ether
Alkali-soluble oils
Indicates path of an ether extract.

***Fig. 1. Class Separation of Benzene-Soluble Materials***

color. To determine the nature of the materials which were not extracted by ether the acid solution was distilled to dryness. The yellow inorganic salts, which had a vanillin odor, were extracted with ethanol. Vanillin, melting at 80–80.5°C. (capillary), after repeated recrystallizations from water, ether-ligroin, and water, was obtained from the ethanol extract. The 2,4-dinitrophenylhydrazone [melting point 269–270°C. (capillary)] gave no depression in a mixed melting point with the hydrazone prepared from authentic vanillin. The estimated yield of vanillin from the oxidation was 3.7 grams.

*Analysis.* Calculated for vanillin, $C_8H_8O_3$: C, 63.16%; H, 5.26%. Found: C, 63.24%; H, 5.50%.

*Analysis of Bicarbonate-Soluble Fraction.* Since Pearl (*5*) found that the lead salt of vanillic acid was soluble when an aqueous solution of acidic materials was treated with neutral lead acetate, this technique was applied and further extended to the separation of the above fraction. The procedure which was used on the aliquot is schematically outlined in Fig. 2.

*Fraction A*, which consisted of a brown oil (4.05 grams) containing crystals, was sublimed under reduced pressure (0.07 mm.) in an oil bath maintained at 90°C. The sublimate consisted of 3.2 grams of a cream-colored crystalline solid melting at 187–192°C. after being washed with ether. The crystals were resublimed at 90°/0.04 mm. and yielded 2.94 grams of a product melting at 193–198°. The material was dissolved in water, treated with carbon black, and recrystallized to a constant melting point of 207–208° C. (capillary). A mixed melting point determination with authentic vanillic acid gave no depression.

*Analysis.* Calculated for vanillic acid, $C_8H_8O_4$: $CH_3O$, 18.44%. Found: $CH_3O$, 18.40%.

*Fraction B.* Upon sublimation of the 2.16 grams of red-brown oil at 100–140°C./0.06–0.08 mm., 0.68 gram of an orange oil resulted. A crystalline product was obtained from the oil by repeated precipitations of an ether solution of the oil into petroleum ether, recrystallization of the soluble portion from water, extraction of the crystals with 8% sodium bicarbonate solution, and microsublimation. The small yield of resulting acidic crystals melted at 201–228°C.

*Fraction C.* The red-brown viscous oil (0.58 gram) was sublimed at 100°C./0.07 mm. A crystalline product was obtained from the sublimate, consisting of 0.35 gram of a yellow-green viscous solid, by precipitating an ether solution of the sublimate into ligroin and recrystallizing from the clear ligroin solution. Further recrystallizations from water, dilute ethanol, and ligroin yielded white crystals with a constant melting point of 129–130°C. (capillary).

*Analysis.* Calculated for $C_9H_9O_2$: C, 72.49%; H, 6.04%. Found: C, 72.84%; H, 6.04%.

A neutralization equivalent of 145 was obtained by titrating a micro sample (2 mg.) potentiometrically with 0.002 *N* alkali. The course of the titration indicated a possible lactone structure. A green color was formed with ferric chloride; however, the presence of phenolic hydroxyls was not confirmed by infrared absorption analysis. A comparison of the infrared absorption of the unknown compound with that of coumarin and cinnamic acid is given in Table VI. These

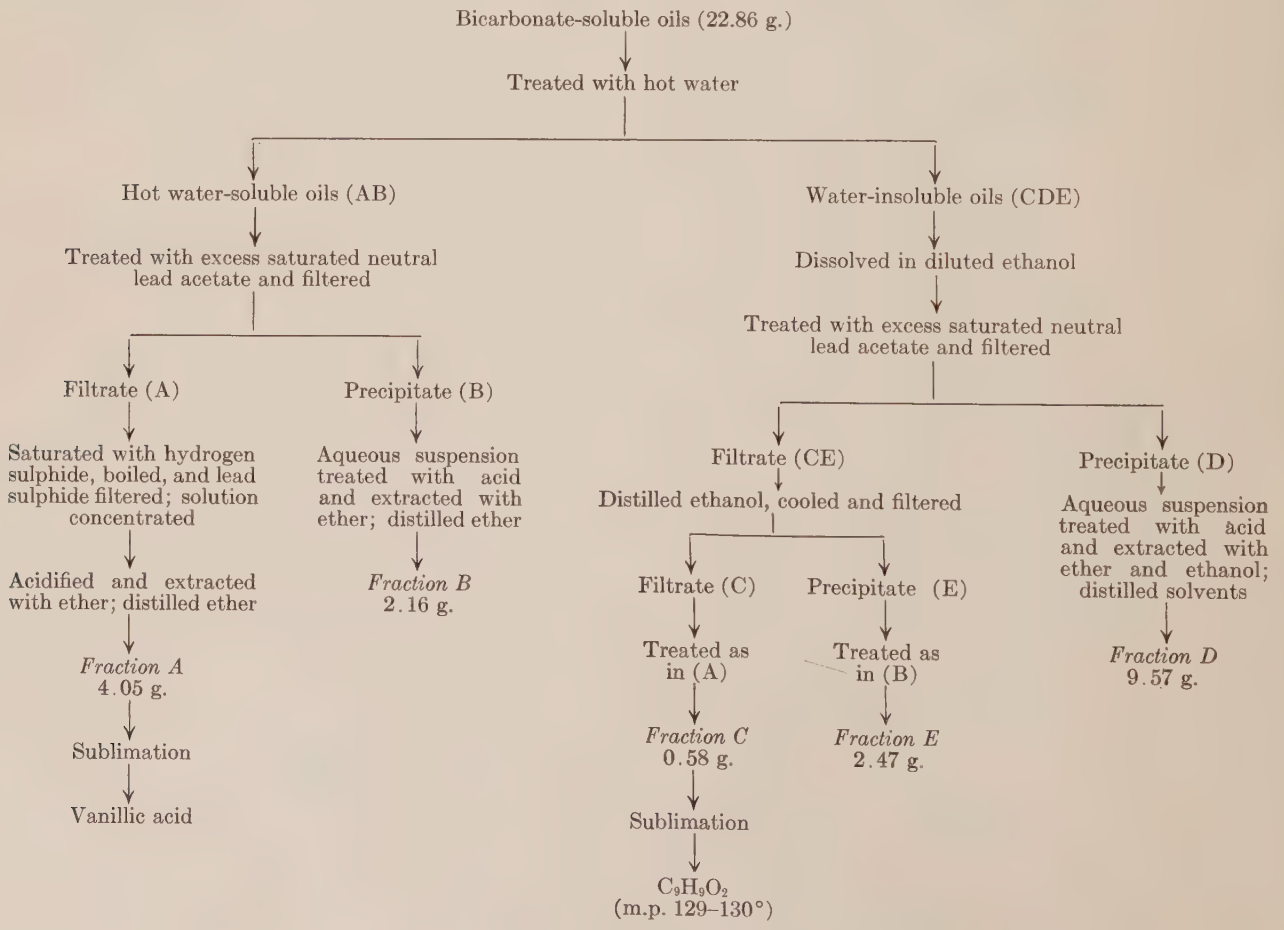
Bicarbonate-soluble oils (22.86 g.)
Treated with hot water
Hot water-soluble oils (AB)
Water-insoluble oils (CDE)
Treated with excess saturated neutral lead acetate and filtered
Dissolved in diluted ethanol
Treated with excess saturated neutral lead acetate and filtered
Filtrate (A)
Precipitate (B)
Filtrate (CE)
Precipitate (D)
Saturated with hydrogen sulphide, boiled, and lead sulphide filtered; solution concentrated
Aqueous suspension treated with acid and extracted with ether; distilled ether
Distilled ethanol, cooled and filtered
Aqueous suspension treated with acid and extracted with ether and ethanol; distilled solvents
Acidified and extracted with ether; distilled ether
Fraction B 2.16 g.
Filtrate (C)
Precipitate (E)
Fraction A 4.05 g.
Treated as in (A)
Treated as in (B)
Fraction D 9.57 g.
Sublimation
Fraction C 0.58 g.
Fraction E 2.47 g.
Vanillic acid
Sublimation
C9H9O2 (m.p. 129–130°)

***Fig. 2. Fractionation of bicarbonate-soluble materials***

**Table VI. Comparison of Analysis by Infrared Absorption**

| *Absorption band* | *Coumarin* | *Cinnamic acid* | *Unknown, $C_9H_8O_2$* |
|---|---|---|---|
| Hydroxyl group | Absent | Present (as carboxyl) | Absent |
| Carbonyl group | Present (as lactone) | Present (as acid, conjugation not indicated) | Present (same as cinnamic acid and at same frequency) |
| Unsaturated aliphatic group conjugated with another unsaturated group | Present | Present | Present (at same frequency as cinnamic acid) |
| Phenyl group | Present (only in one of two regions) | Appears degenerate | Identical with cinnamic acid |
| Lactone (assuming 4- to 6-membered ring) | Present | Absent | Absent |
| Anhydride | Absent | Absent | Absent |
| Unassigned region of 2330–2350 cm.$^{-1}$ | Present | Absent | Present |

analyses indicate a close resemblance of the unknown and cinnamic acid, except in the hydroxyl region and in the region of 2330 to 2350 cm.$^{-1}$ where the compound resembled coumarin. The exact structure of the compound could not be determined because of the small yield.

*Fraction D.* An attempt to sublime (90°C./0.14 mm.) the 9.57 grams of black tar yielded only a trace of a liquid with a plumlike odor. Distillation using an immersion distilling head at 160°C./0.04 mm. failed to produce additional quantities of the oil.

The black tar was only slightly soluble in ether but soluble in ethanol, acetone, dioxane, and glacial acetic acid. Precipitation of a glacial acetic acid solution of the tar into ice water produced a brown muddy precipitate. On filtering, a brown ligninlike powder was obtained. The sublimate was fractionated by the difference in water solubility of the two crystalline components. The product which was more soluble in water yielded fine white needles which melted at 109–111°C. after microsublimation. The oil, which was less soluble in water, gave white crystals melting at 130–148°C. after microsublimation. The aqueous solution of both crystalline materials was strongly acidic.

*Analysis of Sodium Hydroxide-Soluble Fraction.* The scheme of fractionation of the 25.6-gram aliquot of the sodium hydroxide-soluble materials is given in Fig. 3. The 18.9 grams of dark viscous ether-soluble oil, on distillation under reduced pressure, gave the following fractions. At a bath temperature of 160°C. and a pressure of 0.22 mm., 1.63 grams (fraction B) of light brown oil distilled. This fraction was followed by 4.35 grams (fraction C) of a red oil which solidified to a yellow solid. Neither fraction had a constant boiling point. The bath temperature was raised to 180°C. to remove all the yellow solid. To obtain fraction D, the residue was heated with a Bunsen flame, and an additional 1.50 grams of dark oil was obtained by the use of an electrically heated fractionating column. The distillation was discontinued when white fumes, which indicated decomposition, were evolved.

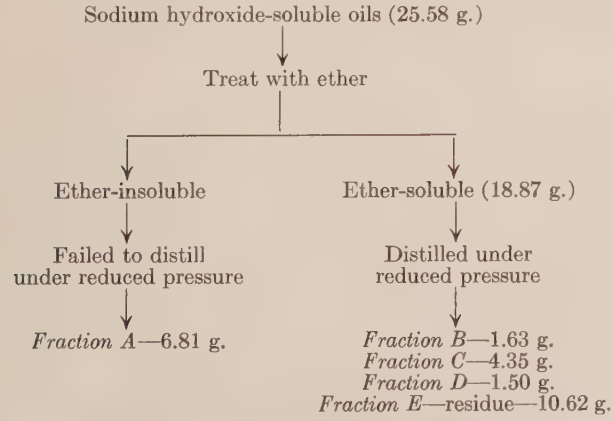


***Fig. 3. Fractionation of sodium hydroxide-soluble materials***

Efforts to form crystalline derivatives of the oily fractions B and D failed. The following reagents were used: benzoyl chloride, 3,5-dinitrobenzoyl chloride (in anhydrous pyridine), and 1-naphthyl isocyanate.

The yellow solid (4.35 grams) obtained in fraction C melted at 80–96°C. and was purified by sublimation at 80°C./0.03 mm. to yield 3.8 grams of a white solid melting at 102–112°C. Recrystallizations from dilute ethanol and ligroin yielded white needles melting at 113.5–114°C. A mixed melting point with authentic acetovanillone was not depressed. Acetovanillone benzoate was prepared by shaking with benzoyl chloride and sodium hydroxide and the resulting derivative was recrystallized from ethanol to give long fibrous needles melting at 102°C. and not depressing a mixed melting point with authentic acetovanillone benzoate.

*Analysis.* Calculated for acetovanillone benzoate, $C_{16}H_{14}O_4$: C, 71.04%; H, 5.19%. Found: C, 71.12%; H, 5.30%.

In an analogous qualitative large-scale oxidation, in which a portion of the oxidized kraft black liquor was lost during the steam distillation of the acidified reaction mixture, a sodium hydroxide-soluble fraction was obtained in the same manner. This fraction was distilled at 180°C./0.3–0.7 mm. The distilled oils were separated physically from the acetovanillone which solidified in the receiving flask. These oils were further fractionated by distillation under reduced pressure. The fractions which were obtained are listed in Table VII.

A portion of each of the above fractions was treated with each of the following reagents: benzoyl chloride, 3,5-dinitrobenzyol chloride, *p*-nitrobenzoyl chloride, and acetic anhydride.

In general, the derivatives obtained were oils. A small amount of a crystalline 3,5-dinitrobenzoate was obtained from fraction B. After a single recrystallization from ethanol, a tan powder melting at 76–85°C. was obtained. The methoxyl content was 8.31%.

A crystalline benzoate was obtained from fraction C.

**Table VII. Fractions from Sodium Hydroxide-Soluble Materials**

| *Fraction* | *Boiling point* | *Nature* |
|---|---|---|
| A | 116°/0.17 mm. | Yellow oil |
| B | 160°/0.24 mm. | Orange oil |
| C | 188°/0.24 mm. | Viscous orange oil |
| D | Residue | Dark tar |

Table VIII. Nitrobenzene and Reduction Products Recovered

| | Grams as nitrobenzene | Yield, % |
|---|---|---|
| Nitrobenzene | 2184 | 65.1 |
| Aniline | 779 | 23.2 |
| Azobenzene | 137 | 4.1 |
| Residue | 23 | 0.7 |
| Total | 3123 | 93.1 |

After shaking the orange oil with benzoyl chloride and sodium hydroxide, the oily derivative which formed was extracted with ether. During the extraction, a brown precipitate, which was insoluble in sodium hydroxide or ether, was formed. The precipitate was filtered and recrystallized from dilute dioxane and ethanol. The powdery yellow-brown crystals melted at 173–174°C. and had a methoxyl content of 11.92%.

*Analysis.* Calculated for $(C_7H_6O_2)_x$: C, 68.85%; H, 4.92%. Found: C, 68.26%; H, 5.11%.

Assuming one methoxyl group in the molecule, the formula weight calculated from the percentage of methoxyl is 260. This would make the above formula $(C_7H_6O_2)_2$ or $C_{14}H_{12}O_4$, which has a formula weight of 244. Since the above formula permits the substitution of only one benzoyl group, the formula of the original phenolic compound may be $C_7H_8O_3$ or a multiple of this formula. A search of the literature failed to disclose a phenol ($C_7H_8O_3$ or $C_{14}H_{16}O_6$) with the benzoate melting at 173–174°C. Attention was given to the monomethyl ethers of trihydroxybenzene which have the above formula.

Extraction of the alkaline reaction mixture from the large-scale oxidation gave 14 liters of a dark amber benzene solution of unreacted nitrobenzene and its reduction products. This benzene solution was extracted with 5% hydrochloric acid to remove aniline. The benzene was distilled from the remaining benzene extract and nitrobenzene and azobenzene were recovered by distillation under reduced pressure. The yields of the above products are summarized in Table VIII. The percentage yield is based on the 3360 grams of nitrobenzene used in the oxidation.

The nitrobenzene reduction products from the small-scale oxidations were not completely analyzed, but the presence of nitrobenzene, aniline (yields up to 32%), azobenzene, azoxybenzene, and sodium *p*-azobenzenesulphonate (SPABS) was indicated.

The SPABS was formed only under superatmospheric conditions. Pearl (*4*) obtained SPABS as a reduction product from the action of sulphite waste liquor and alkali on nitrobenzene but only under atmospheric conditions. In a series of experiments, Pearl (*6*) also proved that the formation of SPABS must result from the reduction of nitrobenzene by lignin in alkaline solution with the subsequent sulphonation of the reduced product in an active state by inorganic sulphites. One of these experiments indicated that an isolated alkali lignin (Meadol) in the presence of inorganic sulphite will reduce nitrobenzene to SPABS.

To determine whether lignin is responsible for the formation of SPABS when kraft black liquors are used or whether the inorganic constituents of kraft black liquor alone will bring about the formation of SPABS, a series of oxidations were made using a simulated black liquor composed only of the various inorganic salts customarily found in kraft black liquor. This study indicated that the two reducing agents—i.e., sodium sulphide and sodium thiosulphate—are mainly responsible for the formation of SPABS in the reaction between kraft black liquor and nitrobenzene. These reducing agents accomplish a simultaneous reduction and sulphonation of the nitrobenzene. The presence of sodium sulphite is not required for the sulphonation.

In the small-scale oxidations, varying amounts of sodium oxalate precipitated with the sodium *p*-azobenzenesulphonate from the alkaline oxidation reaction mixture. An analysis was made of the 18.5 grams of precipitate obtained in oxidation 13. The alkaline precipitate was dissolved in the minimum quantity of hot water. Ethanol was added to the brown aqueous solution and the gray precipitate was filtered. Additional ethanol was added to the filtrate until a precipitate was no longer obtained. The red filtrate contained the SPABS. The gray precipitate was crystallized from water and dilute ethanol and treated with carbon black to yield 11.3 grams of a white powder. The benzyl isothiourea derivative of this powder melted at 193–194°C. and did not depress a mixed melting point with di(S-benzylthiuronium) oxalate prepared from authentic sodium oxalate.

*Analysis.* Calculated for $Na_2C_2O_4$: C, 17.91%; Na, 34.33%. Found: C, 17.91%; Na, 34.07%.

## GENERAL DISCUSSION

In this fundamental study of the reaction between nitrobenzene and kraft black liquor, the first phase involved a determination of the conditions for the optimum yields of lignin degradation products. Previous investigators in the field of lignin oxidation concerned themselves chiefly with obtaining high yields of vanillin. Since guaiacol compounds other than vanillin have been isolated from lignin and since it was not practicable to make a complete analysis of all the products formed in each small-scale oxidation, it was necessary to obtain a fraction which would contain the various guaiacol compounds and afford a comparison of the degree of oxidation obtained. Because compounds of the above type are generally soluble in ether or benzene, an extract obtained with the above solvents would represent the degree of oxidation attained. It was later found that benzene extracted a smaller amount of oils and, therefore, all yields were reported as benzene-soluble materials. A typical example of the difference in the amount extracted by ether and benzene is oxidation 8 in which 66.4% of ether-soluble but only 31.2% of benzene-soluble materials were obtained.

Although a variety of conditions were studied in an attempt to obtain high yields of benzene-soluble materials, the oxidation was not successful from a practical standpoint. The inherent character of the kraft lignin appeared to resist oxidation. This resistance to oxidation may be due to either or both of the following: (1) substitution of sulphur into the lignin molecule, either as a mercaptan or a sulphide, may inhibit oxidation; (2) the lignin during the alkaline cooking conditions is subjected to a reducing action which may alter the lignin molecule and make it less susceptible to oxidation.

Even under drastic conditions, as in the oxidations at 200°C., decomposition of the lignin was difficult. Judging from the smaller amount of precipitated lignin

and the darker color of the acidic filtrate obtained in these drastic oxidations, the lignin may have been degraded only into lower molecular weight polymers without yielding lower molecular weight guaiacol derivatives, or the simple products which may have been formed were recondensed into acid-soluble polymers. These lower molecular weight polymers also composed the greater part of the benzene-soluble fraction of all the oxidations. This is evidenced by the various ligninlike fractions which were isolated from the benzene-soluble materials from the large-scale oxidation.

A similar type of degradation of the lignin may take place under kraft cooking conditions. However, the products in the two cases are not necessarily the same but both may be formed as a result of alkaline hydrolysis. Extraction of the acidified unoxidized kraft black liquor yielded 28.9% of benzene-soluble materials. The nature of these materials was not investigated. The methoxyl content of 10.1% demonstrated that they originated principally from the lignin. The benzene-soluble materials represented a recovery of 20.5% of the methoxyl in the black liquor. Hägglund (*7*) found acetovanillone in kraft black liquor in an amount of about 0.1% of the wood weight, which is further evidence that kraft lignin is severely degraded under alkaline cooking conditions.

The determination of the nature of the ether-soluble extract obtained from the alkaline black liquor was not within the original scope of this work. Since both liquid and solid materials with a mercaptan odor (actually identical with the kraft odor) were obtained, there is a possibility that these materials also originated from the lignin. Further investigation of these materials may lead to a better understanding of the chemistry of the kraft process. Removal of these substances by a more practical means may also solve the kraft odor problem. After a long period, the ether-extracted black liquor regained the original kraft odor to a lesser degree, which indicates that these odoriferous substances can be formed by internal reaction or decomposition.

Nitrobenzene oxidation of the kraft black liquor also destroys the mercaptan odor. In general, the oxidation reaction mixtures had an ammonia or nitrobenzene odor. After the ether or benzene extraction of the nitrobenzene products, the extracted reaction mixture retained only the odor of the solvent. After evaporation of the solvent, no odor remained. Since mercaptan materials were not found in the extract of the nitrobenzene reduction products, the mercaptans were probably completely oxidized.

The benzene-soluble yields were also devoid of a mercaptan odor. However, the benzene-soluble materials gave a qualitative sulphur test after the crystalline sulphur was removed. This indicates that sulphur may have been chemically combined with the lignin fragments which were extracted with benzene. A negative nitrogen test indicated that there was no condensation between the nitrobenzene products and benzene-soluble lignin degradation products. An examination of the sulphur-containing oil which sublimed with the vanillic acid from the bisulphite-soluble materials failed to disclose the nature of the chemical combination of the sulphur in the oil.

The presence of inorganic sulphur compounds in the black liquor had far-reaching effects on the oxidation. The study of the variables of the reaction showed that a much higher ratio of nitrobenzene was required in this study than was required for the oxidation of sulphite waste liquor (*2*, *4*). This was due to the reducing action of the inorganic salts, chiefly sodium sulphide and sodium thiosulphate, which were present in the black liquor. The effect of these salts on nitrobenzene was forcibly demonstrated in the study made on the formation of sodium *p*-azobenzenesulphonate. It is believed that the oxidation of these salts preceded or, at any rate, was accomplished with less difficulty than the oxidation of the lignin. However, their presence in the reaction mixture had no deleterious or retarding effect on the oxidation of the lignin if a large excess of nitrobenzene was used. This was demonstrated by the fact that the yield of benzene-soluble materials was not increased by substituting an alkaline solution of Indulin for the black liquor. On the contrary, the appreciable decrease in yield from Indulin (compare oxidations 8 and 18) leads to the belief that materials other than lignin in the black liquor may exert a beneficial catalyzing action on the oxidation. Inasmuch as only one oxidation was made on Indulin, the above cannot be stated as a definite conclusion. The fact that the methoxyl content of the benzene-soluble products from the Indulin oxidation was in the same range (less that the methoxyl content of lignin) as that of the black liquor oxidations dispels the belief that the benzene-soluble materials from the black liquor oxidations contained a large proportion of black liquor extractives, such as fats, waxes, and resins. The presence of substances with a low methoxyl content in the benzene-soluble fraction may be accounted for by the fact that demethylation of products may have occurred. This loss of methoxyl was not apparent in the methoxyl balance for the large-scale oxidation.

Although nitrobenzene is classified as a mild oxidizing agent, the combined effect of high temperature and the presence of alkali may result in extreme degradative action as indicated above. Additional signs of degradation were observed in the case of the small-scale oxidations made at 200°C. These oxidations yielded a ligninlike precipitate in the alkaline reaction mixture. The precipitate obtained in oxidation 13 was composed mainly of sodium oxalate. The large yield which was obtained indicated that either the lignin or, more probably, the lignin oxidation fragments were severely degraded, or a degradation of the sugar acids present in black liquor occurred. Presumably both took place, but the former may account for the accompanying low yields of benzene-soluble materials in these drastic oxidations. Although the precipitates from the other oxidations were not analyzed, their appearance and solubility to some extent in water led to the belief that they also contained a large proportion of sodium oxalate. A smaller amount of sodium oxalate was probably formed in the less drastic oxidations. Although no attempt was made to determine the nature of the liquid products, the presence of acetic acid and formic acid was suspected.

In addition to the variables which were studied, it was found that the degree of oxidation is also a function of the amount of agitation during the oxidation. This was demonstrated by the much lower yield of benzene-soluble materials obtained in the large-scale oxidation.

The yield in the large-scale oxidation was 17.6%, whereas a yield of 31.2% was obtained in oxidation 8. The only difference between the two oxidations, apart from the quantity used, was the type of autoclave (more satisfactory types were not available) used and, consequently, the degree of agitation. This also partially accounts for the extremely low yields of crystalline oxidation products isolated from the large-scale oxidation. The atmospheric oxidations were made with rapid stirring, but failed to give high yields of benzene-soluble materials. However, it is believed that the yields could be greatly increased by more rapid agitation and/or a longer reaction time.

The two main crystalline products obtained from the oxidation of lignin were vanillic acid and acetovanillone. The combined yield of vanillic acid from the bicarbonate- and bisulphite-soluble fractions was 25.3 grams (7.9 and 17.4 grams, respectively) or 1.8% based on the lignin. The yield of acetovanillone from the sodium hydroxide-soluble fraction of the benzene-soluble materials was 9.4 grams or 0.66% based on the lignin. Vanillin was isolated from an analogous large-scale oxidation which, because of the loss of a portion of the reaction products, was carried out qualitatively. This vanillin was isolated in an unconventional manner, since it was obtained from the acidified bisulphite waste solution from which the bisulphite-soluble materials were supposedly extracted with ether. Evidently the vanillin was not liberated because of the evolution of sulphur dioxide being continually generated from the decomposition of some product in the boiling acid solution. The vanillin was finally isolated by distilling the acidified bisulphite solution to dryness and extracting the residue with ethanol. That vanillin is a product of the oxidation of kraft black liquor was also indicated in a small-scale oxidation made under the same conditions as oxidation 1. In this case, an aliquot of the bisulphite extract was treated as above for the removal of the sulphur dioxide. The vanillin was then precipitated as the 2,4-dinitrophenylhydrazone. From the weight of the derivative which had a methoxyl content of 8.50% (theoretical methoxyl content, 9.34%) the yield of vanillin from this oxidation was calculated to be 6.4%. This value for vanillin may be high, as it may include some acetovanillone which is also soluble in bisulphite solution and also forms a 2,4-dinitrophenylhydrazone under the conditions employed.

The bisulphite-soluble fraction from the quantitative large-scale oxidation yielded vanillic acid instead of the vanillin which was expected. This may be attributed to any of several causes. It is possible that some vanillic acid may have been extracted by the bisulphite solution, or the vanillin, which is readily susceptible to oxidation, may have been oxidized to vanillic acid during the sublimation treatment. Another explanation, which is based on the extremely long time required for the complete sublimation of the vanillic acid from the oily bisulphite-soluble extract, is that the vanillic acid was the result of decomposition of a low molecular weight polymer of lignin. The actual possibility of the latter was investigated by a cursory analysis of the sulphur-containing oil which sublimed with the vanillic acid. The nature of this compound was not definitely established because of the low yield.

An additional amount of vanillic acid was isolated from the bicarbonate-soluble fraction using the procedure developed by Pearl (*5*) which is based on the solubility in aqueous solution of the lead salt of vanillic acid. Since a large portion of the bicarbonate-soluble fraction was insoluble in water, the technique was further extended to afford a fractional separation of the remaining water-insoluble materials by dissolving and precipitating the lead salts from a dilute ethanol solution. In this manner five fractions were obtained from the bicarbonate-soluble materials. Crystalline materials were obtained from all the fractions except one. With the exception of vanillic acid, these crystalline materials were not completely identified because of their small yields. Fraction C, which embraced the compounds whose lead salts were soluble in dilute ethanol and remained in solution after the alcohol was distilled, yielded a white crystalline compound on sublimation which had the empirical formula $C_9H_8O_2$ and melted at 129–130°C. Analysis, which was incomplete, indicated that this compound resembled in some respects the structure of cinnamic acid and coumarin. Three additional crystalline compounds were isolated from the various fractions of the bicarbonate-soluble materials. Extreme difficulty was encountered in the purification of these compounds. This fact coupled with the small yields made it possible to report only the method of isolation and the crude melting points. A further investigation of the structure of the above compounds isolated in larger amounts may be of invaluable aid to the understanding of the chemistry of lignin.

The sodium hydroxide-soluble materials were fractionated according to their solubility in ether. The ether-soluble materials were further separated into more distinct fractions by distillation under reduced pressure. Although these phenolic materials had a definite guaiacol odor, acetovanillone (whose yield was reported above) was the only compound definitely identified. The other phenolic materials were oils which did not boil under reduced pressure at any definite temperature. Also, crystalline derivatives could not be obtained from these oils, with the exception of two compounds. One yielded a small amount of a tan powdery 3,5-dinitrobenzoate which melted at 76–85°C. and had a methoxyl content of 8.31%. The other was a yellow-brown powdery benzoate which melted at 173–174°C. and had a methoxyl content of 11.92%. This benzoate had the empirical formula $C_7H_6O_2$. The assembled data demonstrated that the original phenolic compound may have the empirical formula $C_7H_8O_3$. An insufficient amount of the derivative was available to prove this by saponification and further analysis.

The formation of sodium *p*-azobenzenesulphonate is discussed in another article.

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Received May 23, 1951. A portion of a thesis submitted in partial fulfillment of the requirements of The Institute of Paper Chemistry for the degree of Doctor of Philosophy from Lawrence College, 1950. This work was carried out under the direction of Irwin A. Pearl.

# ASSOCIATION NEWS AND EVENTS

## *Fibrous Agricultural Residues Committee*

There will be no fall meeting of the Fibrous Agricultural Residues Committee in 1951. This was decided by a majority vote of the committee membership. The round-table discussion on strawboard mill problems scheduled for this meeting will be held during the Annual Meeting of the Technical Association of the Pulp and Paper Industry to be held at the Commodore Hotel, New York, N. Y., on Feb. 18–21, 1952.

## *Joint Textbook Committee*

Harry S. Spencer of the Howard Smith Paper Mills, Beauharnois, P. Q., has been appointed Chairman of the Joint Textbook Committee of the United States and Canada. Mr. Spencer succeeds George E. Williamson (deceased) of the Strathmore Paper Co., West Springfield, Mass.

The other members of the committee are: R. S. Hatch, Consultant, Monterey, Calif.; Douglas Jones, Secretary-Engineer, Technical Section, Canadian Pulp and Paper Association, Montreal, P. Q.; R. G. Macdonald, Secretary-Treasurer, Technical Association of the Pulp and Paper Industry, New York, N. Y.; and Royal S. Kellogg, Bradenton, Fla., Secretary.

## *Plastics Conference*

The Plastics Conference will be held at the New York State College of Forestry, Syracuse, N. Y., on Nov. 8 and 9, 1951, instead of the earlier dates previously announced.

## *Fourdrinier Committee*

During the 1952 Annual Convention of TAPPI, the Fourdrinier Committee is planning to hold three "Reservation and Working Seminars."

Attendance at these meetings will necessarily have to be limited due to the nature of the subjects to be covered, as well as the desire of the Committee to have these meetings conducted on a strictly informal discussion basis.

Requirements for attendance at any of these meetings have been set up as follows:

1. The individual must be employed by a mill that is operating fourdrinier machines.
2. The individual should write R. G. Macdonald, Secretary-Treasurer of TAPPI, 122 E. 42nd St., New York 17, N. Y., signifying his intentions of attending the meeting, or meetings of his choice, and to participate in the discussion.
3. Upon receipt of the individual's letter he will be forwarded a questionnaire by TAPPI that will serve as the basis of the discussion during the meeting. This questionnaire should be filled out and returned to TAPPI not later than Jan. 15, 1952, to permit summarizing the data obtained for discussion during the meeting.
4. Those individuals who have complied with conditions 1–3 above will then be eligible for attendance at the meeting or meetings.

The reservation meetings to be held during the 1952 Convention are listed below:

1. Tissue Machine Table Arrangement and Operating Conditions (Tissue Subcommittee).
2. Importance of Shake.
3. Paper Defects—Causes and Cures.

From the information developed through the questionnaires and the meetings, the Fourdrinier Committee hopes to be able to arrive at some of the fundamentals of fourdrinier machine operation. Those mills that completed and returned the Shake Questionnaire during 1950–51 are eligible to send a representative to the meeting on Importance of Shake.

The identity of the mills that respond and answer the questionnaires will remain confidential.

NOEL R. PHILLIPS, *Chairman, Fourdrinier Committee*

## *Pulp Bleaching Monograph*

In a recent mailing of the Technical Association members were advised that the book on Pulp Bleaching being prepared by the Pulp Purification Committee is approaching completion.

Since this book will not be of interest to all members of the Association it will be sent to members who write a letter to the Secretary of the Technical Association of the Pulp and Paper Industry, 122 E. 42nd St., New York 17, N. Y., requesting that a copy be sent to them when it is ready. There will be no charge to members for this book and all members are welcome to request copies. The book will be fairly large and will be expensive to publish. Consequently, it is desirable to limit the number of copies printed to the number desired by Association members.

## *Sixth Engineering Conference of the Pulp and Paper Industry*

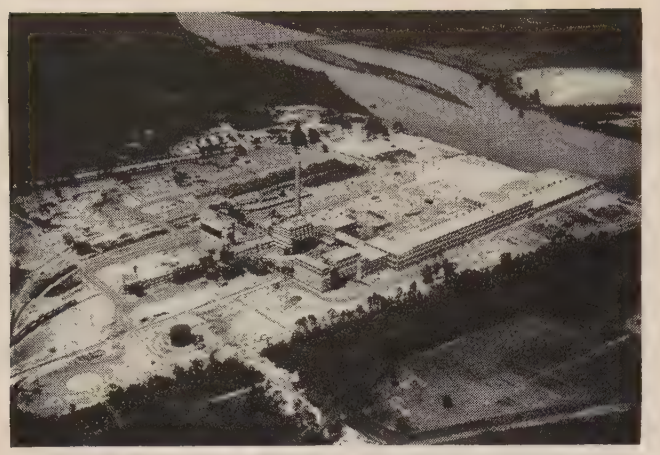
A feature of the TAPPI Engineering Conference to be held at Savannah, Ga., on Oct. 15–18, 1951, will be a visit to the mill of the Southern Paperboard Corp. at Port Wentworth, Ga. This visit will be made in addition to visits to the mill of the Union Bag & Paper Corp. and the Herty Foundation Laboratory in Savannah.

The mill of Southern Paperboard Corp., at Port Wentworth, Ga., has been in operation since June 15, 1948. The mill was designed to produce an average of 450 tons of liner board and similar products per day. The supporting manufacturing facilities are such that the full capacity of the 236-inch paper machine can be obtained.

The new mill is located about seven miles northwest of the City of Savannah at Port Wentworth, on a tract of land containing some 180 acres, facing the Savannah River and adjacent to Southern Coastal Highway No. 17. Rail service is available from the Savannah and Atlanta Railway, connecting with all of the other lines running into Savannah, and deep water shipment can be made from the mill from its own dock, which also provides for the receipt of incoming materials.

Process water for the mill is furnished from the filter plant of the Savannah Industrial and Domestic Water Supply System, which furnishes Southern Paperboard Corp. with a minimum of 10 million gallons per day of clear, potable, soft water.

Preliminary investigations for the location of the mill were started in 1945 and most of the principal equipment was purchased during March and April of 1946. Actual construction may be said to have started with the driving of the first concrete pile on Nov. 4, 1946. The first steel was received in April of 1947 and was erected by December of the same year,



***General view of the Southern Paperboard mill, Port Wentworth, Ga.***

by which time the majority of the buildings had also been housed in.

The buildings generally are of steel frame with concrete foundations, floors, and grade beams; 8-inch brick curtain walls; corrosion proof sash; and all the foundations carried on concrete piling averaging 25 feet in depth. The roofing is of precast light concrete slabs with insulation where required.

The following gives some idea of the scope of buildings and the approximate amount of materials used therein; total ground area, 270,000 square feet; building volume, 10 million cubic feet; 4422 piles; 4300 tons of steel; 21,000 cubic yards of concrete; $1^3/_4$ million board feet of lumber; 75,000 square feet of sash; 3 million brick; and 1000 tons of pipe.

The general facilities provided for the operation of the mill are as follows:

### Wood Preparation and Handling

The wood yard is arranged for the storage of about 25,000 cords received by rail, water, or truck, in such a way that the handling into or out of storage is within the range of locomotive, crawler, or truck cranes.

Three steel conveyors, parallel with the railroad tracks, carry the wood to two by 45-foot barking drums, the rossed wood from which will be delivered onto a sorting conveyer for the cleaning or rejection and return of unbarked wood, the clean wood being sent to two 88-inch, ten knife chippers, the chips from which go by belt conveyer over four chip screens to a ground storage chip bin having 24 hour capacity.

The storage bin is of steel construction with large openings on the bottom to prevent arching of the chips. Feeders from these openings will deliver chips onto a belt for distribution of the proper amount of wood into each digester after passing through a weightometer. In this manner, the wood chips from any section of the bin can be delivered to any of the digesters, as desired.

Bark and sawdust from the yard is collected on conveyers and sent to a bark burning boiler. Special provision has been made for cleaning the bark from under the conveyors and for the storage and reclaiming of surplus refuse.

### Digesters

For the cooking of the wood chips, there are six welded steel digesters, each having a capacity of over 10 tons of pulp per charge. Any of these six digesters can deliver into either of the two blow tanks, so that two classes of cooks with separate woods can be made at the same time.

Full automatic control from the operating floor of the digester building provides for the delivery of chips, the cooking cycle, the blowing, and the relief discharge, the latter being condensed for the recovery of turpentine.

The steam discharged from each digester blow is passed through a separating cyclone and thence through a heat reclaiming system where it will be condensed and used as a medium for heating clean, incoming water for wash purposes.

### Wash Room

For the deliquoring of the pulp, two lines of vacuum type washers are provided. One of these lines consists of four 8 by 14-foot washers for the removal of liquor from the quick cook or base stock requirements; and the second line consists of three 8 by 10-foot washers.

The washers are set at the same elevation as the digester room operating floor, with the drop legs carried down to round horizontal tanks extending into and through the wash building with the various liquor pumps placed under the tanks. Full provision has also been made for the removal of foam and the collection of soap.

Vibrating type preknotters are placed ahead of the washers in order to improve the mat formed on the cylinders, with resulting economy in washing. The rejected knots are taken by gravity through a small jordan for breaking up and return through the system; any further rejects ultimately coming out with the tailings from the centrifugal screens.

The washers are provided with hoods for the removal of vapor and a full complement of automatic control instruments, including consistency regulation and metering of the incoming stock. For ease of erection and removal of cylinders, a hand-operated crane is installed above the washers; and a small elevator will serve the digester and wash room floors.

The final washed stock discharges by gravity into two 15-ton concrete storage chests, one for each line; and agitation is obtained by propellers.

While the operating floor of the wash room is closed in and conditioned, open or canopy construction is used for the underlying section.

### Screen Room

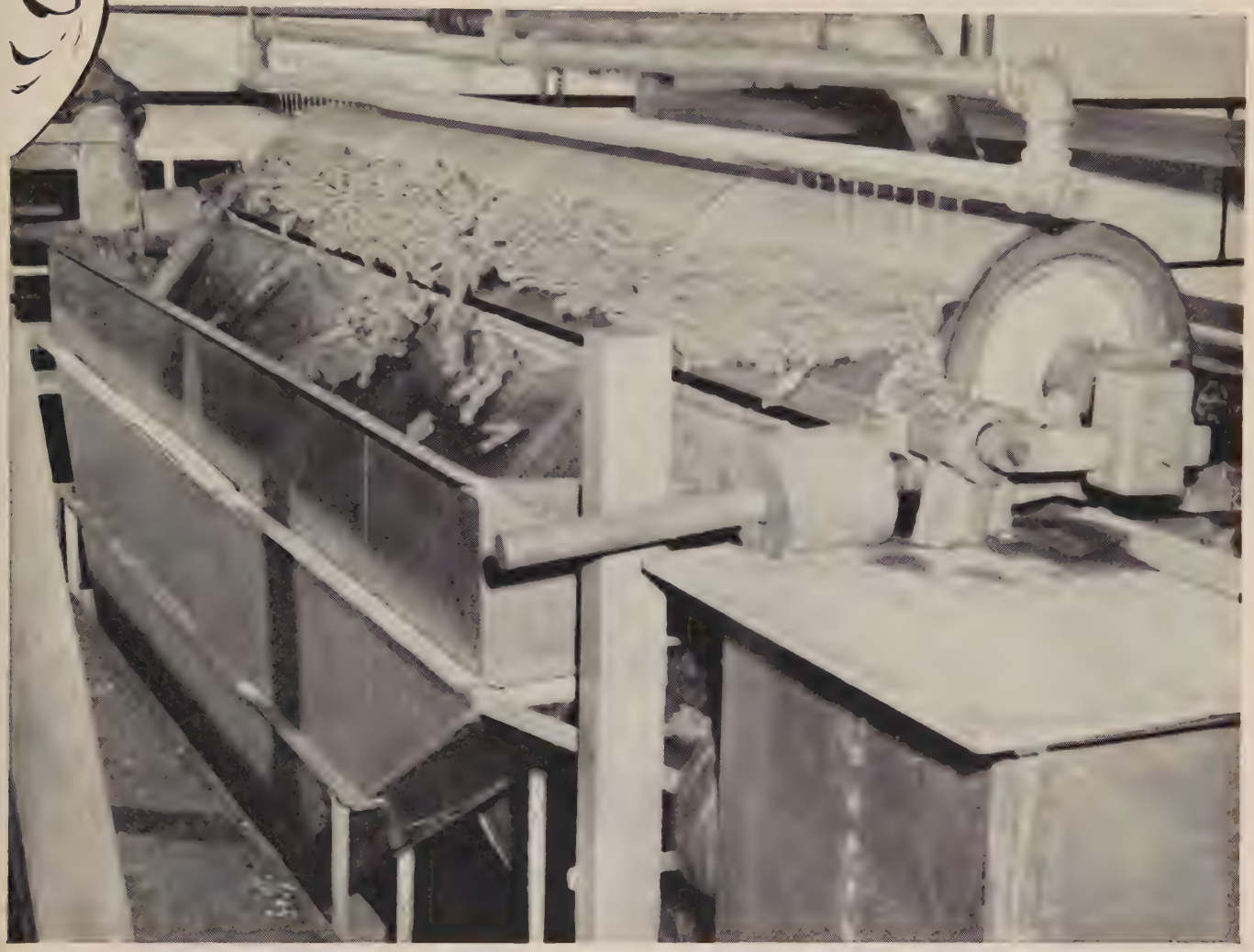
The two classes of stock from the two washed stock storage chests are pumped through independent mix tanks, volume meters and consistency regulators to a flow box feeding six centrifugal screens, arranged so that as many screens as are desired may be apportioned to either stock with a seventh screen common to the tailings from both.

The final rejects and tailings from these centrifugal screens flow by gravity through a thickener into a small surge chest, from which they will be pumped through a refiner and returned into the base liner washed stock chest.

The accepted stock from the centrifugal screens flows by gravity to three 8 by 12-foot vacuum deckers, two of which will thicken the stock for the base liner and deliver by gravity into a screened stock storage chest of 20-ton capacity. The third thickener will be used in conjunction with the second line of washers and screens for delivery into a similar separate chest.

***The office building of the Southern Paperboard Corp.***

# A SIGHT TO GLADDEN THE EYE OF EVERY HARD PRESSED PAPERMAKER



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*South East view of power building*

White water from the thickeners is carried by their drop legs into separate concrete storage tanks placed under their respective stock chests. Separate white water recirculating pumps are provided for each chest.

### Refining

For the final preparation of the stock before going on to the paper machine, fourteen jordans with 400-hp. motors are installed and interconnected to give the maximum of flexibility in respect to the requirements for each grade of pulp.

Normally eight of these jordans are used for hydrating the base stock and three for the secondary stock, discharging into their respective concrete storage chests, from which they are pumped through finishing jordans, with two on the base stock and one on the secondary. A separate chest is also provided for gum or hardwood pulp with provision for separate refining and final combining of the two pulps ahead of the fan pumps delivering to the paper machine.

Arrangements for consistency regulation ahead of the jordans and a close control of the latter by instrumentation is included. The size and alum are received, stored, and applied in liquid form.

The refining room building is served by a 5-ton overhead crane.

### Paper Machine

The 236-inch high-speed fourdrinier kraft liner board machine is of the most modern type and arranged for speeds up to 1600 feet per minute.

The flow box is a three-pass, streamlined design, with 120-inch slice.

The fourdrinier part carries a wire 120 feet long and 236 inches wide, arranged for installing from the tending aisle without necessity of removing the fourdrinier proper. The breast roll is 28 inches in diameter; table rolls, $10^1/_2$ inches;

*View of log conveyor discharge to barking drum*

there are ten 12-inch suction boxes and a special double box, suction couch roll 44 inches in diameter, having one suction box 7 inches wide and the other 12 inches. Included also is a secondary headbox unit for applying a top film of stock to the base sheet; also the latest type high-speed, duplex shake with two units.

There are two press sections, each with a rubber-covered upper roll 30 inches in diameter, and a rubber-covered lower roll of the suction type 36 inches in diameter, all connected with a pneumatic type loading system to properly distribute weight on the bottom rolls as desired.

The drier part is arranged in four sections with twenty 60-inch driers in each; six 60-inch felt driers in the first two sections and two similar in the third and fourth; and all journals are of extra heavy duty, self-aligning rollers.

The driving train is fully enclosed with all driers in the lower tier of each section horizontally connected together by intermediate idler gears which, in turn, drive the upper driers by means of idler pinions, all arranged for lubrication by a central oil lubricating system.

Following the driers are two stacks of calenders having eight rolls each, with pneumatic type loading system for applying pressure to the journals at the top of the roll. The first stack is arranged for two water boxes.

Between the two calender stacks there are three 60-inch diameter calender driers.

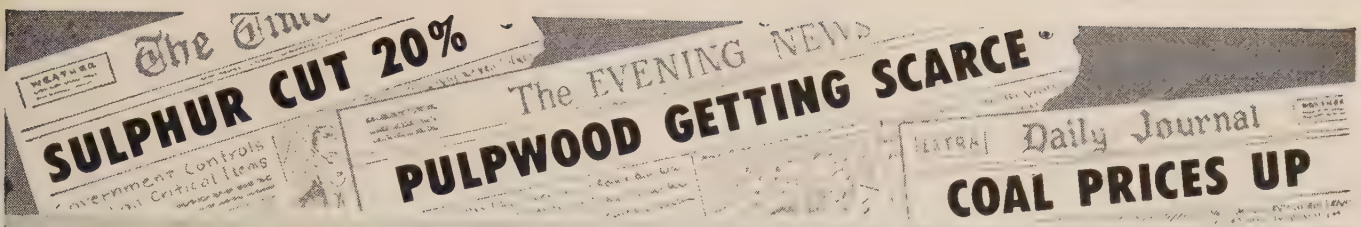
The reel is of the uniform speed type with 42-inch driving drum and six reeling drums.

For the final rolls, a two-drum, uniform speed winder suitable for taking rolls up to 72 inches in diameter is provided, with antifriction bearings throughout and balanced for speeds up to 4000 feet per minute.

The sections of the machine requiring variable speeds are driven by a sectionalized individual motor drive having electronic control, the motors for which obtain their current from

*Barking drums*

*Lime kiln with causticizing plant in the background*

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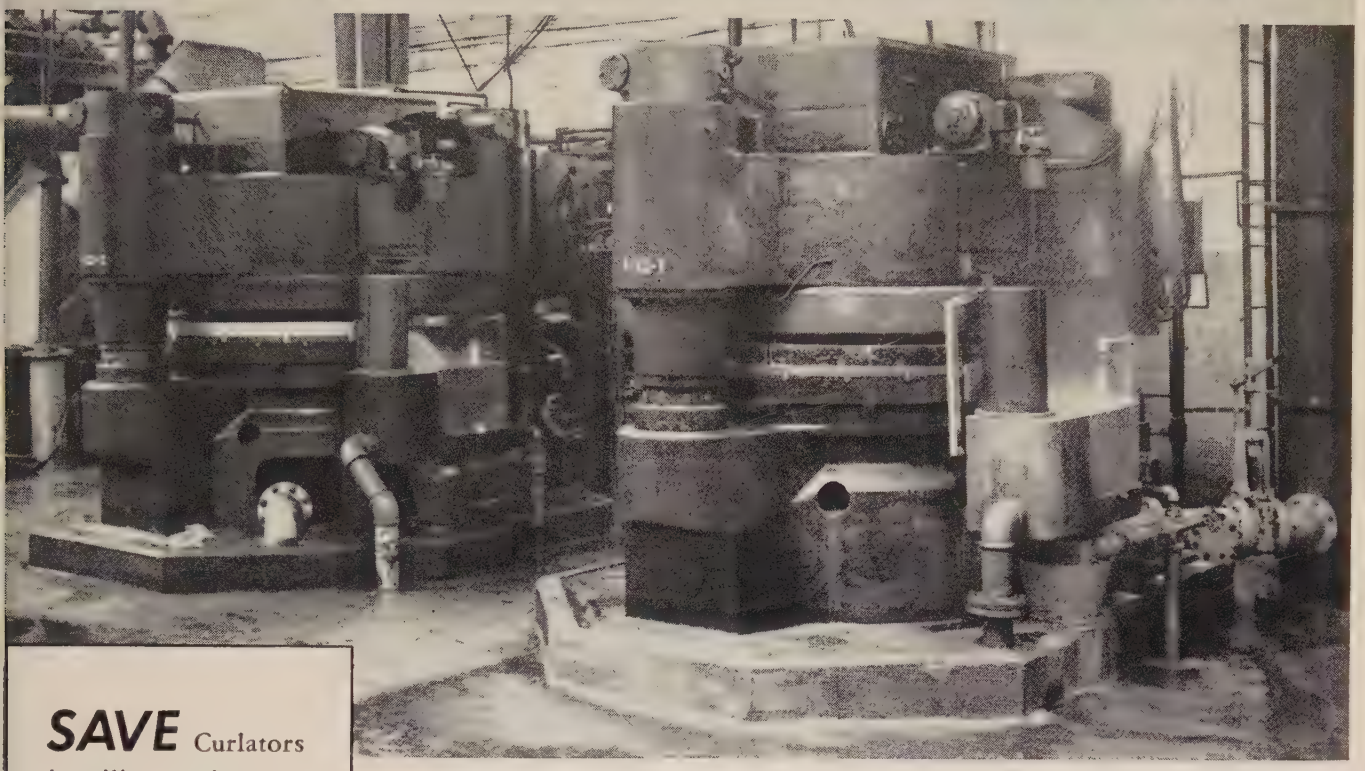

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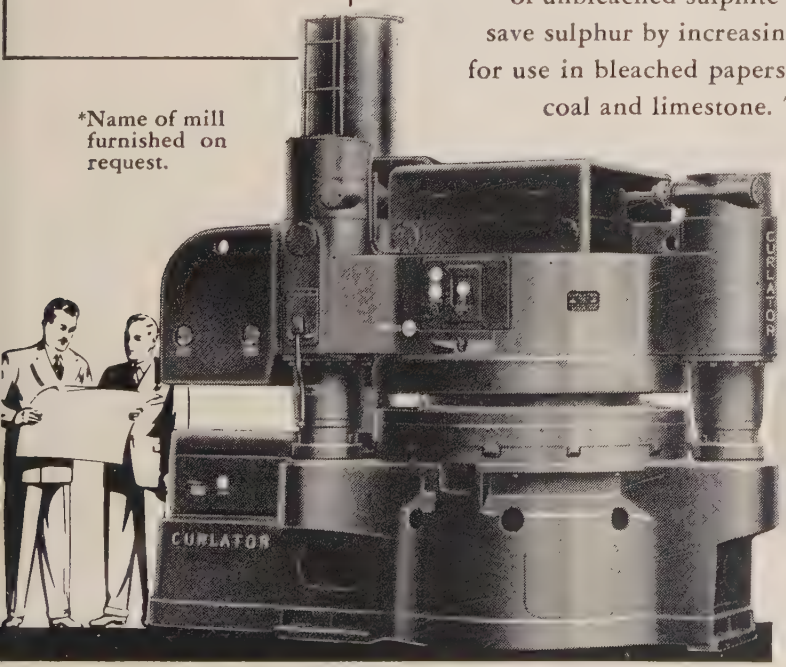
*Name of mill furnished on request.

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T. M. Reg.—Curlator Corporation, Rochester, N. Y.

***Causticizing tanks and loading end of the lime kiln***

two 900-hp. motor generator sets, with a separate generator for each section of the machine.

The winder drive is of the regenerative braking type with a 300-hp. motor generator set and one 150-hp. motor on each of the winder drums.

Air conditioning and removal of vapor from the machine room is accomplished by a transite hood over the drier section, with 11 exhaust fans and two large heater and supply fans providing 75% of the total make-up air requirements.

For obtaining the necessary vacuum on the flat boxes, suction couch, and presses, six vacuum pumps are installed aggregating 1125-hp.

The fan pump for the base stock of the machine is probably one of the largest yet installed, having a capacity of 40,000 g.p.m., and driven by a variable speed motor. The fan pump for the secondary headbox has a capacity of 10.000 g.p.m.

White water recovered from the paper machine and not recirculated is returned to the screen room ahead of the pulp thickeners.

Broke from the paper machine is conveyed to a breaker beater with 64-inch roll for return as pulp to the base liner machine chest.

A full complement of auxiliaries of the latest type is included, for the conditioning of felts, removal of condensate, oiling, instrument control, etc.

The machine room building itself, including its extension for roll finishing, is 630 feet long and 70 feet wide. While it was built to house a single machine initially, it was so designed that it can be readily expanded for a second.

For servicing the paper machine, there is an electrically operated crane running the full length of the building, equipped with two $17^1/_2$-ton trolleys for the handling of the largest rolls to a grinder located in the basement at the dry end of the building. A 15-ton electrically operated crane for the handling of rolls from the reel to the winder and a 5-ton hand-operated crane for the back drive are also included.

Rolls coming off the end of the paper machine are banded and passed in echelon over a floor scale somewhat wider than the full width of the paper machine. From the scales, the rolls pass onto a 12-ton elevator, with 24 by 10-foot platform, for delivery to the basement and into roll storage by tiering lift trucks. This elevator is also large enough to take a lift truck and its load from the machine room floor to the basement if necessary.

Rolls to be rewound are handled by the main crane to a 100-inch rewinder, the finished rolls from which return onto the elevator.

### Laminator

Since the mill was put into operation an 85-inch laminator has been installed. The purpose of this unit is to combine two sheets of kraft liner to make a 90-pound sheet, thus relieving the fourdrinier machine from this type of tonnage.

### Shops and Stores

The machine shop and mill stores building projects toward the railroad track from the dry end of the paper machine, and is provided with a 30-ton trolley crane extending from over the railroad tracks into the machine room so as to provide for handling of rolls or equipment from cars to the machine room crane and distribution to any point. Auxiliary cranes in the machine shop also pick up materials from the basement floor or from the main 30-ton trolley and service the various machine tools which are located on the main floor level. The first floor under the machine shop is used for mill stores and wash room facilities.

The space between the extended fan platform of the machine room and the machine shop is occupied by air-conditioned offices for supervisors, with a maintenance office and drafting room on the upper floor.

### Roll Handling

As a continuation from the machine room and the machine shop toward the river, there is a roll storage building with a capacity for 10,000 tons. This building is 460 feet long on the side paralleling a servicing railroad track in a train shed, and 220 feet wide on the river end fronting a dock built for a channel depth of 32 feet to take care of deep water shipments down the Savannah River and its terminals.

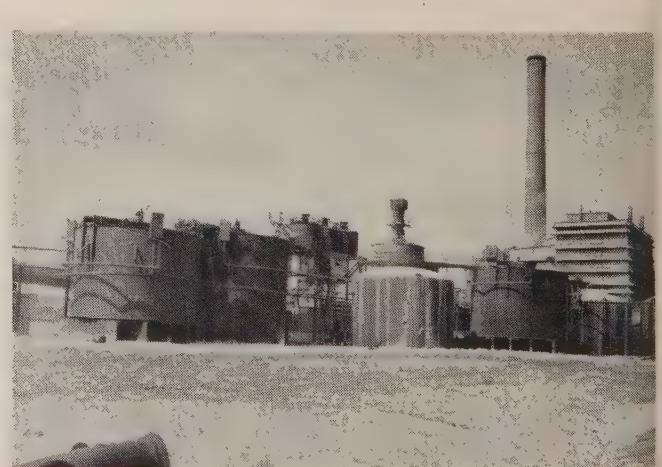
### Recovery of Chemicals

Black liquor recovered from the washing operation is stored in two tanks, 30-feet diameter by 32-feet high, and pumped continuously to a sextuplet long tube black liquor disk evaporator, discharging to concentrated liquor storage tanks, from which it will be pumped through a cascade-type evaporator and finally delivered to spray nozzles for burning in a modern type black liquor recovery and steam generating unit.

There are two of these recovery boiler units, each with a capacity for burning 650,000 pounds of solids per day and generating steam at 625 p.s.i., 700°, to tie in with that generated by the main boiler plant.

The hot waste gases from the recovery boilers, after passing through cascade evaporators, go through two Cottrell electrical precipitators for the recovery of soda that would normally be carried off in these gases. The dry, recovered salt cake from the precipitators is conveyed to a mixing tank where it can be mixed with either the weak wash from the causticizing plant or weak black liquor and built up to sufficient concentration for return into the disk evaporators.

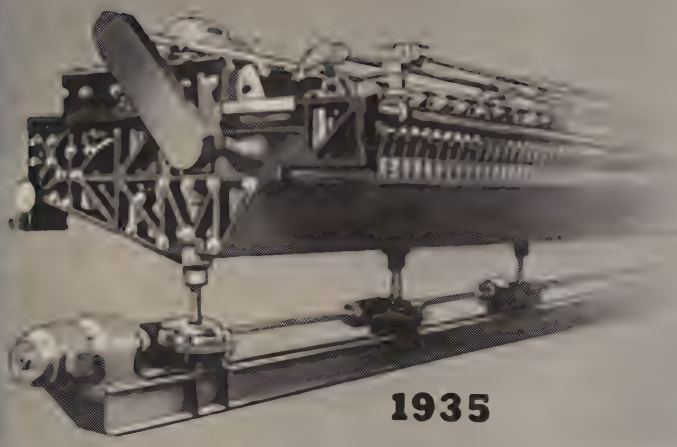
Black liquor soap removed at relatively low concentration from the foam tanks of the black liquor washing operations is taken off and combined with the feed to the sextuplet steam evaporator and then removed again between the effects of this unit for delivery to a tank where the final soap is skimmed off



***View of the causticizing plant***

# PRESSURE INLETS?

PROGRESS in inlet engineering is never-ending at Valley. This progress, over many years, has built up a reservoir of experience which is yours to profit by.



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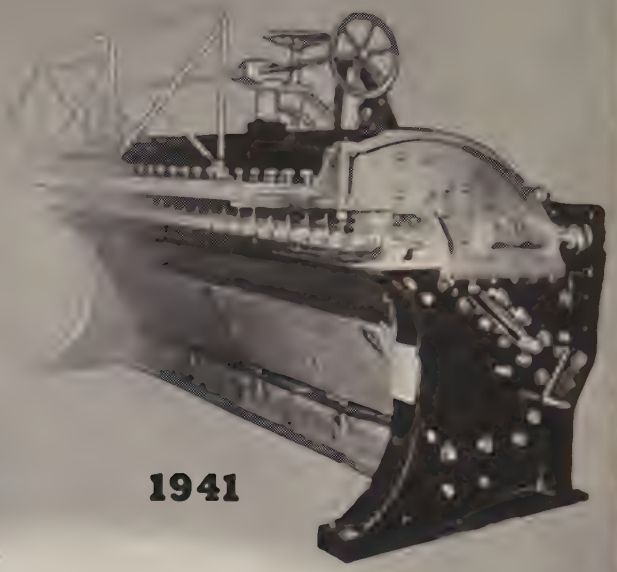

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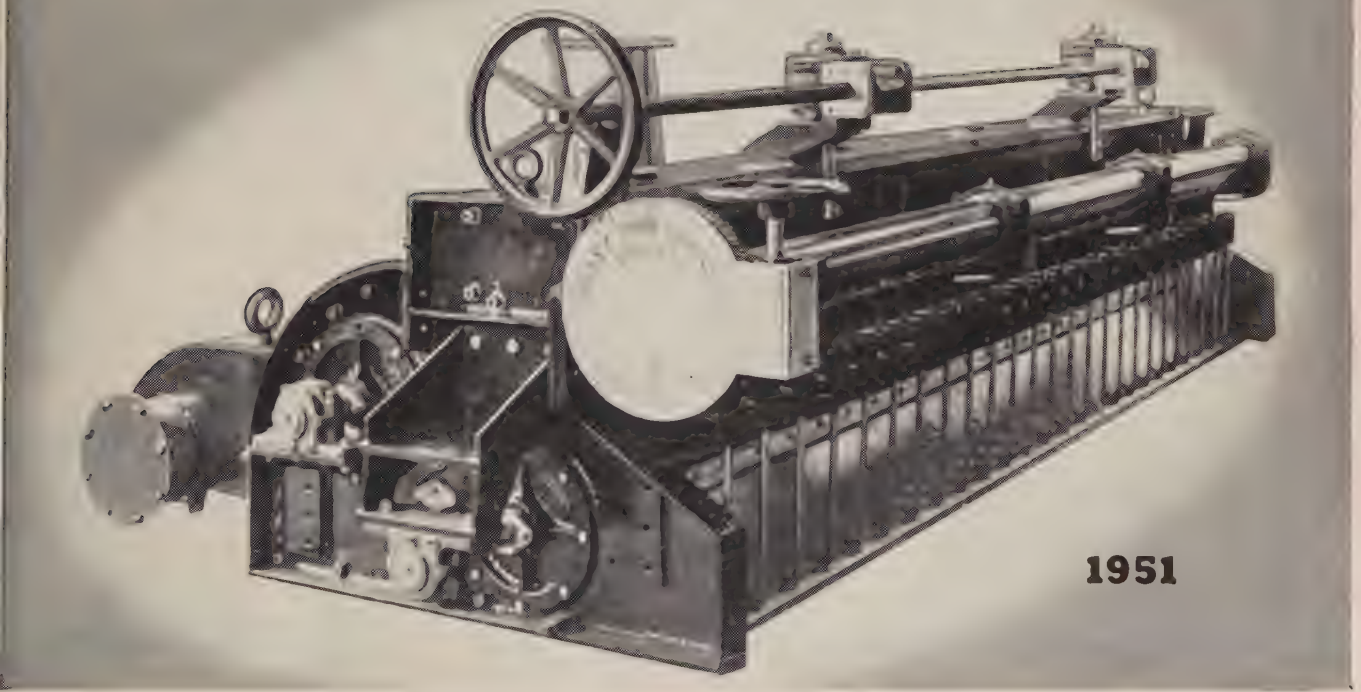
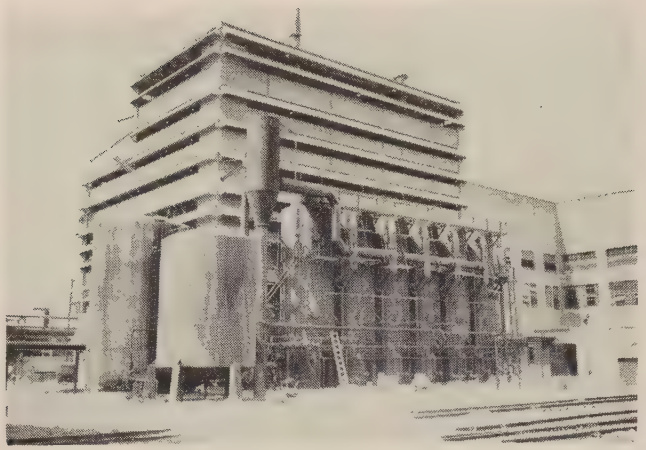


1951

VALLEY IRON WORKS CO.
APPLETON, WISCONSIN



*Evaporators with the recovery building in the background*

and stored for shipment, the excess remaining liquor returning to the evaporators.

Make-up salt cake requirements are handled pneumatically from railroad cars into storage and to the salt cake mixing tanks where it is combined with black liquor feeding into the recovery units.

The multieffect evaporators are of the self-supporting type placed in the open immediately outside the recovery boiler building. The automatic controls are combined with those for the recovery unit and are handled at one centralized point.

The chemicals reduced by the recovery units deliver in the form of molten smelt into dissolving tanks where they mix with recovered weak liquor from the subsequent recausticizing operation.

The green liquor from the dissolving tanks is pumped into two storage tanks, each 36 feet diameter by 24 feet high. Before using this green liquor in the causticizing operation it is clarified in a tray type thickener, 35 feet diameter by 24 feet high, and the resulting dregs from same further washed for the recovery of soda.

The milk of lime from the slaker, after classifying and removal of grits, is pumped to elevated causticizing tanks, 12 feet diameter by 10 feet high, arranged in series and discharging by gravity into a tray-type white liquor clarifier, 35 feet diameter by 24 feet high. The clarified white liquor from this unit returns to two storage tanks, 36 feet diameter by 24 feet high, for reuse in the digesters.

The settled mud from the white liquor clarifier is further washed in a tray-type thickener, 35 by 24 feet, for the recovery of chemicals and the final resulting sludge delivered into a lime mud storage tank, 20 by 20 feet, from which it is pumped over two 6 by 6 vacuum type mud filters for delivery into an oil fired kiln, 8 feet diameter by 300 feet long, thus giving reburned lime for the major portion of that required in the slaking operation.

Provision is made for receiving, delivering, and burning limestone in the kiln as an alternative to using fresh lime as make-up. The small amount of fresh make-up lime required to replace that lost in the relatively closed system can be delivered from railroad cars into a storage tank by a pneumatic handling system and delivered into the slaker in conjunction with the reburned lime in automatically measured quantities continuously.

The weak liquors resulting from the various washings in the recausticizing system are collected and stored in a tank 36 feet diameter by 24 feet high, and recirculated to the dissolving and other liquor tanks, in conjunction with the black liquor recovery unit. The lime dust carried out by the exit gases from the kiln is also recovered by wet processes and returned into the system.

The controls for the continuous causticizing operation are located in an enclosed room near the slaker at about the center of the operations, the balance of the equipment, except for the lime mud filters, being in the open.

### Power Plant

The power plant is divided into three units; that is, boiler room, turbine room, and recovery room. The boiler and turbine rooms are in adjacent buildings; the recovery room being connected to both by a passageway in which auxiliary equipment is located.

The boiler room has two oil fired integral furnace power boilers, each approximately 1500 hp. A third boiler duplicating the two power boilers is provided with a Hofft furnace for burning bark and sawdust. This third boiler is capable of developing the same amount of steam as the power boilers when using oil alone or firing with a combination of oil and wood refuse. The boilers operate with steam at the superheater outlet of 625 p.s.i. and 700°F. total temperature, with a feed water temperature of 230°F.

The burners on all boilers are of the dual type so designed as to burn either oil or powdered coal. Oil, which is to be used initially, can be delivered by barge or tank car to a 12,500 barrel storage tank, 50 feet diameter by 37 feet high, and pumped to auxiliary measuring tanks, one near the boiler house and the other near the firing end of the kiln.

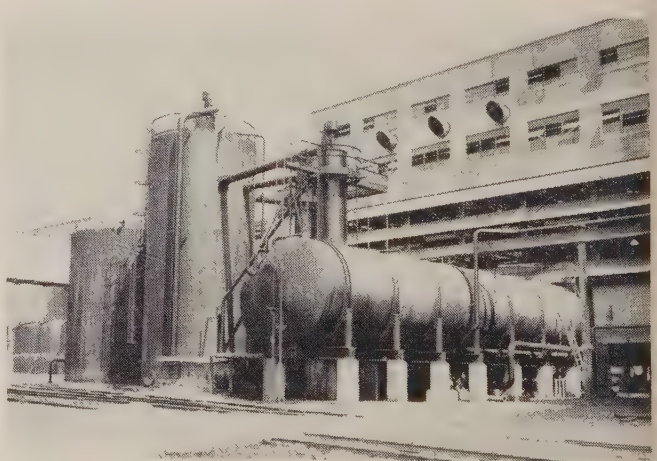
All three of these boilers, together with the recovery unit, discharge their gases into a radial brick stack 250 feet high and 14 feet diameter at the top. This stack is lighted and marked in accordance with the regulations of the Civil Aeronautics Administration.

In the turbine room there are two units; one a 6000-kw. turbogenerator of the extracting, noncondensing type, with steam automatically extracted at 150 p.s.i. and exhausted at 50 p.s.i. The second turbine of the same capacity but of the extracting, condensing type, extracts at 50 p.s.i. and exhausts to a surface condenser at $27^1/_2$-inch mercury. These turbogenerators operate in parallel on a common bus and generate at 4160 volts using steam at 600 p.s.i. and 700°F. at the throttle.

The condenser is of the surface type, two-pass, and with dual water boxes, having a total surface of 7500 square feet.

Installed also in the turbine room are two 100-p.s.i. motor-driven air compressors, each with a capacity of 542 c.f.m. free air, for use in supplying air throughout the mill. Also installed in the turbine room are two 350 p.s.i. air compressors, each having a capacity of 300 c.f.m. free air, for use with the soot removal system.

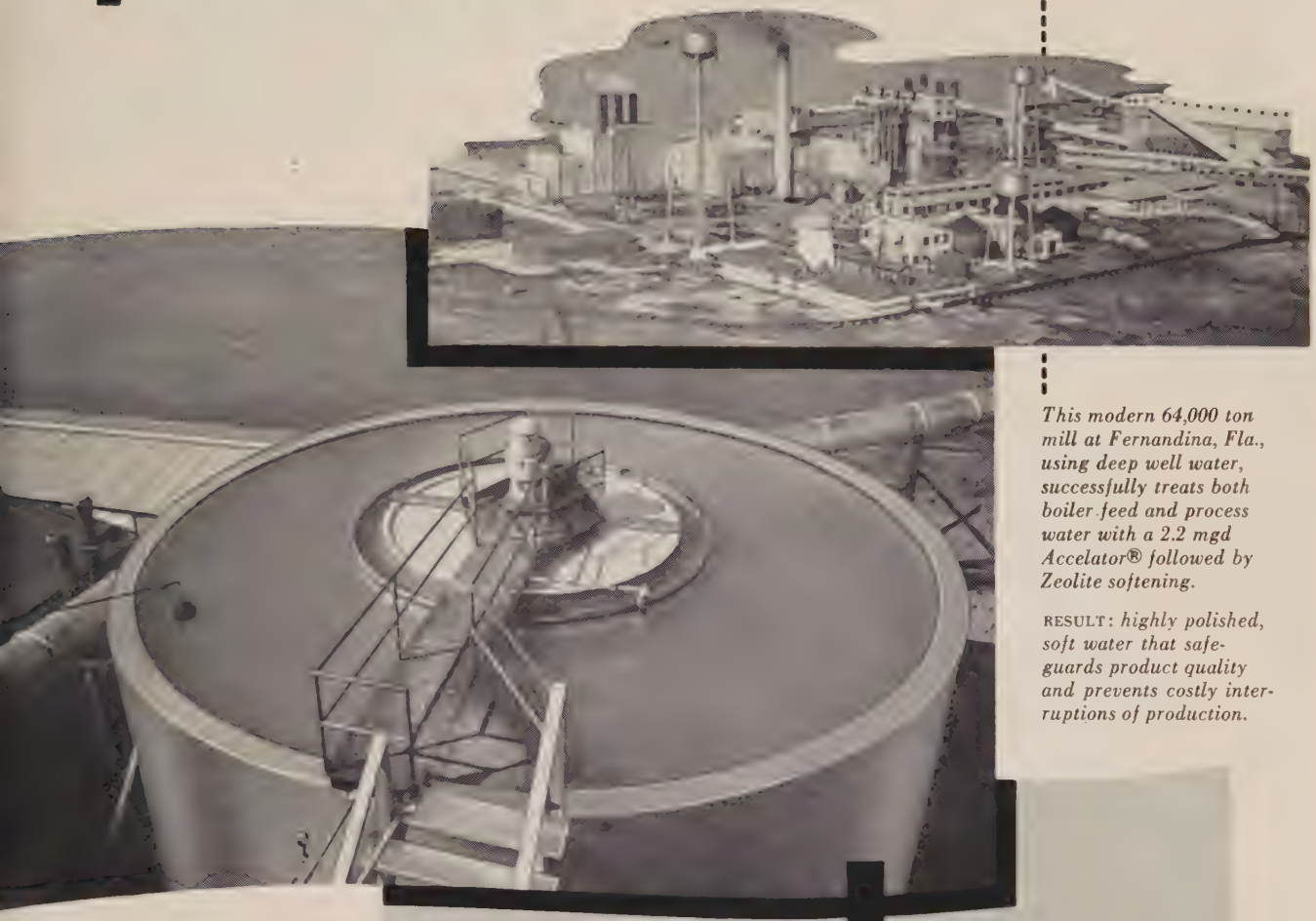
A 600,000-pound per hour horizontal type deaerating heater with vent condenser is installed in the upper part of the connecting building between the turbine room and recovery room. Underneath this heater there are three centrifugal boiler feed pumps, one electric motor driven and two steam turbine driven, with the exhaust steam discharging into the



*View of foam tank, weak black liquor tanks, and washroom in the background*

*this mill uses*

# polished water



*This modern 64,000 ton mill at Fernandina, Fla., using deep well water, successfully treats both boiler feed and process water with a 2.2 mgd Accelator® followed by Zeolite softening.*

RESULT: *highly polished, soft water that safeguards product quality and prevents costly interruptions of production.*

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|---|---|
| HIGH in dissolved minerals, alkalinity, magnesium and calcium hardness | ZERO hardness |
| APPRECIABLE iron and color | ZERO iron and color |
| LARGE AMOUNT of silica present | LOW alkalinity and silica |

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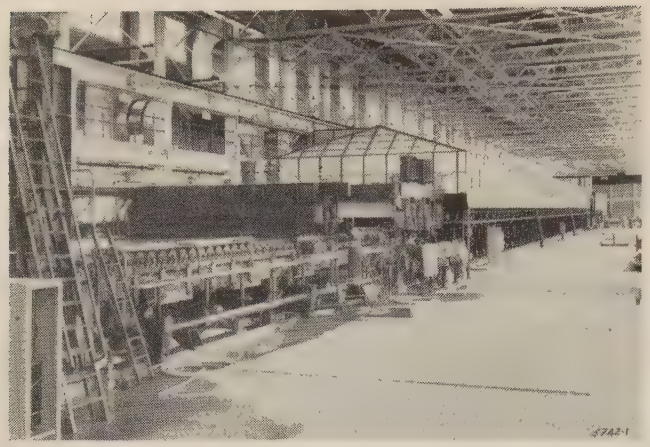
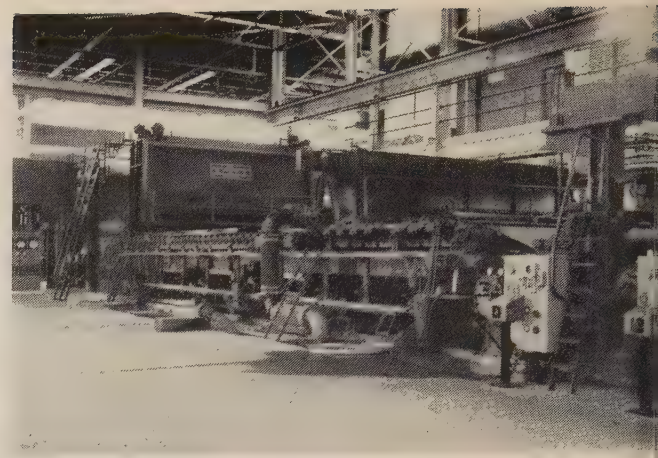


*View of machine from position standing at fourdrinier wet end*



*Wet end showing main headbox and slice, fourdrinier part, and auxiliary headbox*

deaerating feed water heater. The throttle steam for this turbine is taken from the 150 p.s.i. header in the turbine room.

### Electrical Distribution

For the 22,000-hp. installed motor capacity, the electrical distribution is in two voltage level classes. The first or primary system at 4160 volts, 3 phase, 3 wire, 60 cycles, is supplied by the two 6000-kw. turbine-driven generators. It serves direct motors rated 200 hp. and larger, as well as a number of unit type substations. The second or secondary system at 440 volt, 3 phase, 60 cycles, is supplied by the unit type substations, serving motors rated 150 hp. and smaller, and also forming the primary distribution system for building lighting.

The primary distribution is of the radial type, with its control, together with the generator controls, placed in totally enclosed, metal clad switchgear placed in the turbine room and arranged for the outgoing circuits to correspond to the manufacturing departments. Outgoing circuits radiate from the switchgear to strategically placed control rooms wherein are located the unit type of substations and motor starting equipment.

The transformer and secondary distribution controls are combined into load center unit substations wherein the transformer and control equipment are close coupled and all interconnections wholly enclosed.

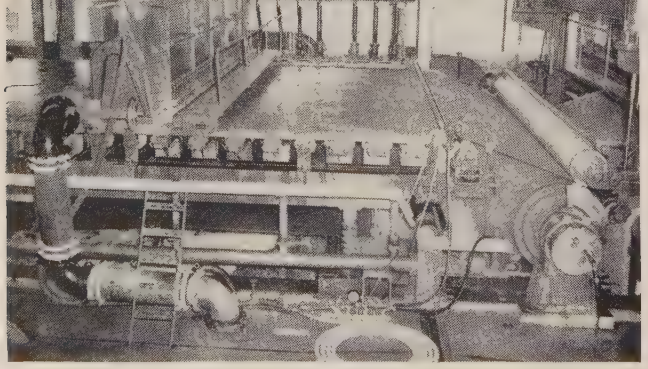
In general, full voltage magnetic starters are used throughout. Those for the 4160-volt motors have oil immersed contacts and are fitted with high interrupting capacity current limiting fuses, all mounted in self-supporting steel enclosures. The 440-volt motor starters are air circuit breaker magnetic combination type, several of which will be grouped together in steel structures known as a motor control center. Both the high-voltage and low-voltage starters are placed either in the same rooms with the load center unit substations or in adjacent rooms. Thus all of this equipment is kept out of the manufacturing areas, out of the way, easily accessible for maintenance, and under control of only authorized persons as well as being fully protected from excessive moisture conditions. Remote control push button stations in watertight cast-iron cases are placed at each machine for the operatives to start and stop the motors.

In effect the low-voltage distribution system consists principally of the circuits from the motor starter to the individual motors, which in addition to others, has the advantage of reducing to a single motor, partial shutdowns caused by trouble that might develop in any one circuit.

Fluorescent lighting is used in those areas where conditions permit; otherwise incandescent lighting is used. The lighting distribution is at 440 volts primary, stepped down to 120/220 volts with small transformers conveniently placed in the manufacturing buildings, and arranged for subdivided control limited to relatively small areas. In addition to the general lighting system, there is a "pilot light" or "Night Watchman Light" system, controlled from the turbine room for use not only during the nonoperating hours of the plant but for emergency lighting in the event of turbogenerator failure.

Provisions have also been made for connection to an outside source of power, to provide current for maintenance purposes and necessary pumps during the nonoperating hours when the turbines would be shut down or the boiler plant under repair.

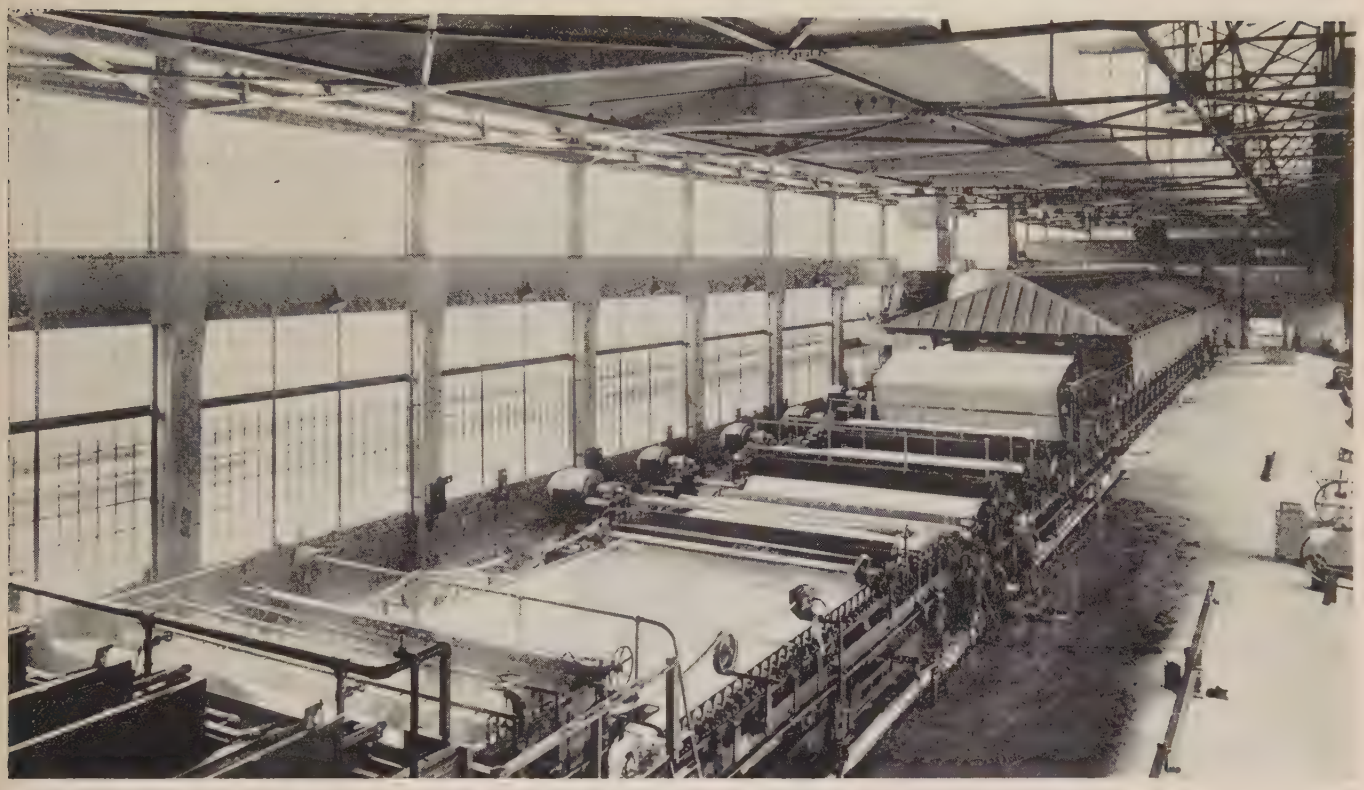
Wiring in general is in rigid metallic conduit, installed ex



*View of top liner stock emerging from auxiliary headbox and passing from suction couch to first press felt*

*View of Simplex press part with sheet leading to first lower drier*

# Now Fenestra's Hot-Dip Galvanizing of Steel Windows Minimizes Maintenance



West Coast Pulp and Paper Mill

Fenestra Steel-Strong Windows are now available hot-dip galvanized and Bonderized. They will stay new under most conditions without painting. Window maintenance is almost eliminated.

The complete galvanizing-Bonderizing process is done in Fenestra's new plant, the only plant in this country designed especially for hot-dip galvanizing steel windows. Bonderizing, after galvanizing, gives the windows a more attractive appearance and prepares them to receive paint when they are used in locations where painting is desired, especially for decorative purposes.

Assembled window frames and assembled ventilators are galvanized separately, before final assembly, to permit all exposed metal surfaces to receive a protective coating. And the Fenestra galvanizing tanks are built large, so the sash can be hung at an angle and completely immersed in the zinc bath in one dip—the protective coating is therefore smooth and uniform. Slow, timed withdrawal from the zinc tanks, to eliminate sags and runs of zinc, is another Fenestra feature.

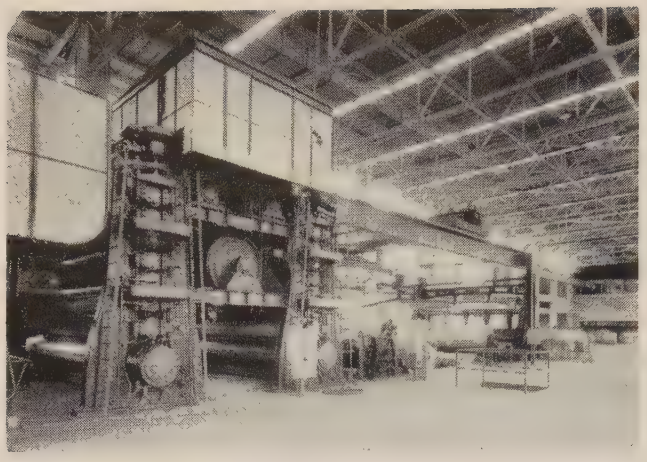
Eight important steps are included in the Fenestra Hot-Dip Galvanizing process: (1) cleaning, (2) pickling, (3) rinsing, (4) fluxing, (5) drying, (6) galvanizing, (7) Bonderizing and rinsing, (8) planned final assembly.

In addition to the galvanized-Bonderized finish, Fenestra Windows are also available with a Bonderized and baked-on prime-painted finish. . . . For complete information, call a Fenestra representative (see "Fenestra Building Products Company" in your Classified Telephone Directory) or write to Detroit Steel Products Company, America's oldest and largest steel window manufacturer.

*Fenestra*

**Hot-Dip Galvanized Steel Windows**

**DETROIT STEEL PRODUCTS CO., 2250 E. GRAND BLVD., DETROIT 11, MICHIGAN**



*View of calender stack followed by reel and winder*

posed on the ceilings, walls, or under trusses, and in wet areas is safeguarded, so far as is practicable, against corrosion. In these areas moisture-resistant insulated wires are also used as a further precaution against trouble developing inside the conduits. To reduce as much as possible work stoppages due to primary circuit failures, each circuit is designed for two complete circuits in parallel, normally to operate continuously in parallel but each of sufficient capacity to carry the load without injurious heating.

### Water Supply

Water for the process requirements in the mill is delivered through a 20-inch line at about 50-feet head from a new filter plant recently constructed by the Savannah Industrial and Domestic Water Supply System. Part of this water is to be taken initially through the surface condenser of the turbine and then boosted to higher pressures for mill requirements. As this water is potable, drinking facilities are provided from the same source in an independent line.

To furnish water for fire protection, evaporator condenser, cleaning of wood, wash-ups, etc., where clean water is not necessarily required a separate pump house takes water from the Savannah River. In this pump house there are two 1000-g.p.m. fire pumps, one motor driven and one gasoline engine driven; and two 5000-g.p.m. for the mill requirements.

Waste disposal for the mill is carried off in two main trunk sewers to the Savannah River, liberal provision being made for general drainage of the area.

A 100,000-gallon elevated water tank is provided for the underground loop system of mains in conjunction with the fire pumps, to provide the necessary hose and sprinkler facilities of the mill.

### General Facilities

The main office building contains some 10,000 square feet of floor area and is fully air conditioned. It is treated architecturally in the Williamsburg style. The building is located on the north side of the property in conjunction with the first aid, clock house, and main entrance gates so that access to the front of the office is obtained without going inside the fence although access is also available to employees to the inside from the rear. Liberal parking space for employees' cars, buses, etc., is provided in the immediate area close to the office. The main entrance highway and grounds in the vicinity of the offices have been landscaped, with young pines.

Full facilities for automatic call, fire alarm, and telephone systems are installed.

Liberal paved roads are located throughout the mill area, and space is also provided for the building of a cafeteria and recreational facilities for employees.

### Management and Personnel

The Southern Paperboard Corp. is a majority controlled subsidiary of Robert Gair Co., Inc., with George E. Dyke, President, R. F. DeVoe, Vice-President; T. W. Earle, Vice-President and Forester; E. O. Sommer, Comptroller; E. Meyer, Treasurer; W. F. Howell, Secretary; William Bergman, Assistant Comptroller; C. R. Bradley, Assistant Treasurer; and R. B. Trotman, Assistant Secretary.

### Engineering

J. E. Sirrine Co., of Greenville, S. C., was responsible from the inception of the project in the prepration of all reports, selection of equipment, designing, and detailing of final plans under the direction of D. G. Moon, head of the Pulp and Paper Department, assisted by R. H. Mills as Project Engineer. Supervision of the actual construction work was in charge of J. W. Cantrell as Resident Engineer.

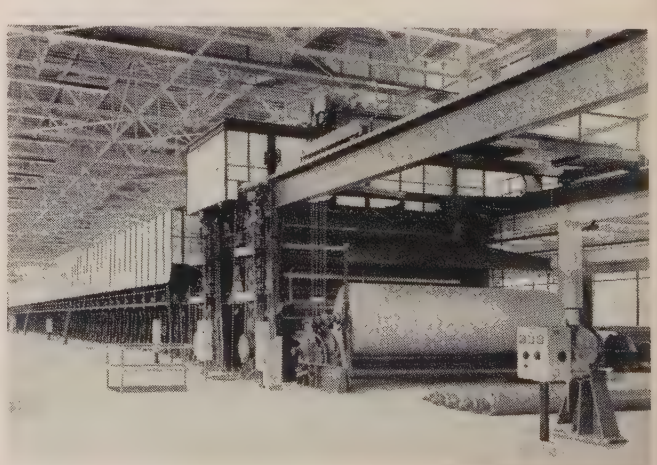
### Woodlands

Gair Woodlands Corp. was organized in 1945 as a wholly owned subsidiary of Southern Paperboard Corp. to acquire timberlands and develop them as a source of supply of pulpwood for the mill at Port Wentworth. T. W. Earle is President of Gair Woodlands Corp., which has purchased approximately 235,000 acres of timberland in South Carolina, Georgia, and Florida. These holdings have been grouped in nine areas, each supervised by an experienced forest engineer, and are being developed under the most approved forest management plan. This includes reforestation, fire protection, and the use of selective cutting methods. Gair Woodlands Corp. in its reforestation program is planting annually from two to three million pine seedlings on its own land.

The area managers are employing approved forest practices in the cutting of timber and are selling at the present the poles, piling, veneer stock, sawtimber, cross ties, dogwood shuttle blocks, mine props, pulp wood and fuel wood, and other timber products. The area managers also offer their services free of charge to adjoining land owners to advise them as to proper timberland management policies that they may follow if they so desire to better their income from their timber lands.

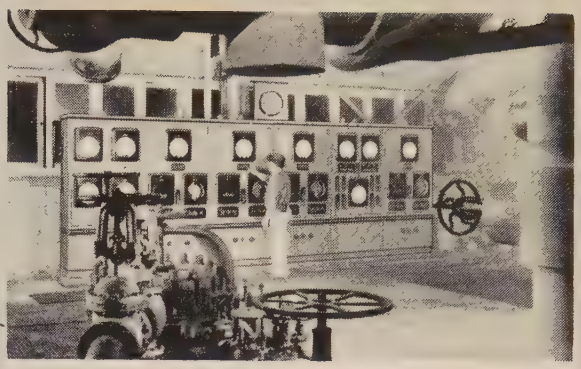
Gair Woodlands Corp. is very active in various national and state organizations to promote better forestry. Among its memberships are included those in Southern Pulpwood Conservation Assn., American Pulpwood Assn., North Carolina Forestry Assn., Georgia Forestry Assn., North Carolina Forestry Assn., Georgia Forestry Assn., Florida Forest and Park Assn., Forest Farmers of America, and the Forest Industries Information Committee.

The Southern Paperboard mill in full operation will consume in excess of 250,000 cords of pulpwood a year, part of which will be obtained from lands owned by Gair Woodlands Corp., and the balance through pulpwood dealers who obtain their wood from farmers and other private timberland owners.



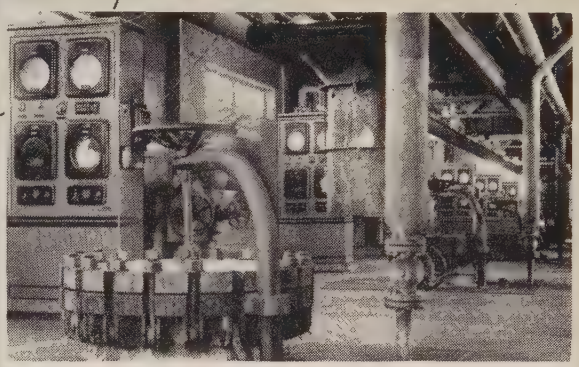
*View of drier section, calender stack, and reel*

**North . .** Marathon Paper Mills of Canada, Ltd.
Marathon, Ontario



**East . .** Brown Company
Berlin, N. H.

**West . .** Weyerhaeuser Timber Company
Longview, Washington



**South . .** Mead Corporation
Kingsport, Tenn.

# Better pulp production comes automatically with FOXBORO Digester Control

Wherever pulp is made, modern digester rooms like the ones shown above are proof that Foxboro Control is the shortest route to better operation.

With this advanced-design control, you can be sure that every cook will follow the exact schedule you want. Steaming and gas-off will be held to the requirements of the individual cook. Pulp quality and uniformity will be improved, with substantial savings in steam and chemicals.

Foxboro Control Instrumentation is available for *all* types of digesters. For detailed information, discuss your problems with the Foxboro engineer in your area, or write to **The Foxboro Company, 7810 Neponset Ave., Foxboro, Mass., U.S.A.**

**FOXBORO**
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**AUTOMATIC DIGESTER CONTROL**

# PERSONAL MENTION

## *Items About New and Old Tappimen*

### *New TAPPI Members*

*Clyde M. Anderson,* Chief Chemist, A.P.W. Products, Albany, N. Y., a 1934 graduate of the New York State College of Forestry.

*Lawrence L. Ardern,* Librarian, College of Technology. Manchester, England.

*Robert J. Askevold,* Division Leader, The Pure Oil Co., Crystal Lake, Ill., a 1934 graduate of the University of Chicago.

*C. J. J. Ninck Blok,* Director of Research, Van Gelder Zonen, N. V., Royal Paper Mills, Velsen, Noord, The Netherlands, a 1939 graduate of the University of Utrecht.

*George J. Bowden,* Chief Chemist, Escanaba Paper Co., Gross, Mich., a 1929 graduate of the University of New Hampshire.

*Gerald W. Burgoyne,* Chemist, National Adhesives (Canada) Ltd., Toronto, Ont., Canada, a 1934 graduate of London University.

*Bennie C. Burish,* Chief Chemist, Badger Paper Mills, Inc., Peshtigo, Wis., a 1948 graduate of the University of Wisconsin.

*Ian M. Chandler,* Junior Chemical Engineer, St. John Sulphite Ltd., Fairville, N. B., Canada, a 1951 graduate of the University of Toronto.

*John E. Cleary,* Chief Chemist, St. Lawrence Paper Corp., Norfolk, N. Y., a 1949 graduate of Brigham Young University.

*Per H. Collin,* Staff Superintendent, Stora Kopparbergs Berglas, A/B, Skutsgar, Sweden, a 1940 graduate of the Royal Institute of Technology, Stockholm.

*William B. Cook,* Technical Assistant, The Champion Paper & Fibre Co., Pasadena, Tex., a 1946 graduate of Iowa State College.

*Joseph P. Corbin,* Chemist, American Cyanamid Co., Calco Chemical Div., Bound Brook, N. J., a 1951 graduate of the University of Maine.

*Dante S. Cusi,* President, Aceite Casa, S. A., Mexico, D. F., Mexico, a graduate of R. Politecnico, Milano, Italy, with an Eng.D. degree.

*Paul F. Del Conte,* Packaging Chemist, National Biscuit Co., New York, N. Y., a 1948 graduate of New York University.

*Frank C. Demshar,* Superintendent, River Raisin Paper Co., Cleveland, Ohio.

*Harry E. Dunholter,* Chief Chemist, Container Corp. of America, Cincinnati, Ohio, a 1936 graduate of the University of Cincinnati.

*Frank D. Elderkin,* Factory Manager, Cozier Container Corp., Jefferson, Ohio. Attended Northwestern University.

*William A. Fannon,* President and Treasurer, The Fannon Trading Co., Appleton, Wis.

*Arthur C. Gault,* Superintendent, Iowa Fibre Box Co., Keokuk, Iowa. Attended Syracuse University.

*Sylvain Ginsbourger,* Editor, *The Paper & Twine Journal,* New York, N. Y.

*Mario Gislon,* Assistant Director, Production Dept., Cartiere Burgo S.p.A., Turin, Italy, a 1929 graduate of Turin University with a ScD. degree in 1938.

*G. W. Gravell,* Librarian, Patent Office Library, London, England.

*Curtis E. Green,* District Sales Engineer, Link Belt Co., Atlanta, Ga., a 1938 graduate of Louisiana State University.

*Robert W. Hagemeyer,* Assistant Manager, Calcium Carbonate Sales, Wyandotte Chemicals Corp., Wyandotte, Mich., a 1949 graduate of the University of Michigan.

*John H. Hall,* Special Representative, Superheater Co. Ltd., Montreal, P. Q., Canada.

*Wadsworth L. Hinds,* Assistant Director of Research, Keyes Fibre Co., Waterville, Me., a 1938 graduate of the Massachusetts Institute of Technology.

*Charles I. Horton,* Sales Engineer, R. T. Vanderbilt Co., Inc., Norwalk, Conn.

*Anthony W. Huberty,* Sales Engineer, Oliver United Filters, Inc., Chicago, Ill., a 1946 graduate of Northwestern University.

*Richard H. Hudson,* Foreman, Pomeroy Mfg. Co., Inc., Vincennes, Ind. Attended the University of Indiana.

*Cheun-Fa Hung,* Engineer, Shihlin Paper Mill, Shihlin, Taipeh, Taiwan, China, a 1941 graduate of Chiao-Tung University, Shanghai.

*Thurston M. Iverson,* Superintendent, Kraft Mill and Bleach Plant, The KVP Co. Ltd., Espanola, Ont., Canada, a 1919 graduate of Shawinigan Technical Institute.

*Louis A. Klein,* Assistant Chemical Engineer, Gulf States Paper Corp., Tuscaloosa, Ala., a 1950 graduate of the Georgia School of Technology.

*Joseph J. Kryszak,* Paper Mill Superintendent, Wisconsin Tissue Mills, Menasha, Wis.

*Theodore Ley,* President, Universal Corrugated Box Machinery Corp., Linden, N. J., a 1936 graduate of Columbia University.

*James W. MacKillop,* Chief Chemist, Works Laboratory, British Vegetable Parchment Mills Ltd., Northfleet, Kent, England.

*Henry G. Maeder, Jr.,* Chemical Engineer in charge of Coating Development, Dixie Cup Co., Easton, Pa., a 1936 graduate of the University of Pennsylvania.

*Roy L. Miller,* Pulp Research, St. Regis Paper Co., Deferiet, N. Y., a 1939 graduate of the University of Maine.

*Robert D. Moynihan,* Bleach Plant and Stock Preparation Superintendent, Finch, Pruyn & Co., Inc., Glens Falls, N. Y.

*Elmer L. Mumma,* General Manager, F. X. Hooper Co., Inc., Glenarm, Md. Attended Johns Hopkins University.

*L. Paul Newton,* Assistant Professor, Western Michigan College, Kalamazoo, Mich., a 1951 graduate of the University of Maine.

*Wilbur R. Noel,* Chemist, Kalamazoo Paper Co., Kalamazoo, Mich., a 1951 graduate of Western Michigan College.

*Paul A. Parker,* Manager, Corrugated Box Div., Anchor Hocking Glass Corp., Lancaster, Ohio, a 1916 graduate of Ohio Wesleyan University.

*John H. Payne,* Head of Sugar Technology Dept., Hawaiian Sugar Planters Assn., Honolulu, T. H., a 1930 graduate of the University of Cincinnati with a Ph.D. degree.

*Roger C. Quick,* Sales Engineer, Eastern Chemicals, Inc., Albany, N. Y., a 1926 graduate of Ohio State University.

*William H. Rambo,* Consulting Engineer, Portland, Ore., a 1921 graduate of the University of Oregon.

*Shri C. R. Ranganathan,* President, Forest Research Institute and Colleges, New Forest (Dehra Dun), U. P., India.

*James H. Rooney, Jr.,* Superintendent, Corrugated Div.,

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His ticket entitles the bearer to one chance in the Remnie paper lottery to be held May 30
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L
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LOTTERY
His ticket entitles the bearer to one chance in the Remnie paper lottery to be held May 30
T
(No.95)
LOTTERY
His ticket entitles the bearer to one chance in the Remnie paper lottery to be held May 30
O
(No.96)
LOTTERY
His ticket entitles the bearer to one chance in the Remnie paper lottery to be held May 30
N
(No.97)

# *Paper Mill Financing 1782 Style**

**Being one of a series of monographs demonstrating the ingenuity of paper makers of yesteryear.*

MANAGING a paper mill in the 18th Century was a serious affair. Paper making was regarded as a sort of public utility, and was held under the watchful supervision of the Government "commissions" of that time. Then government regulations contained many "don'ts" and few helps. As a result, financing was always a problem to paper makers, since the official "grants" rarely carried more than permission to engage in business.

In 1782 the Milton Mill in Massachusetts needed money badly, and got official permission to run a lottery . . . another example of the resourcefulness of paper makers.

Difficulties of one kind or another always seem to have been the unwanted guests of paper manufacturers. Theirs has always been a constant struggle to improve the utilization of men, materials and machinery, to meet an ever-increasing demand for paper.

Pennsalt research chemists eagerly welcome the opportunity to help manufacturers boost production and lower costs. Specific inquiries are invited. *In the East:* Pennsylvania Salt Manufacturing Company, Philadelphia 7, Pa. *In the West:* Pennsylvania Salt Manufacturing Company of Washington, Tacoma, Washington.

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PROGRESSIVE CHEMISTRY FOR OVER A CENTURY

Great Southern Box Co., Inc., New Orleans, La. Attended Loyola University of the South and the United States Military Academy.

*T. Robert Santelli*, Senior Research Chemist, Plaskon Div., Libbey-Owens-Ford Glass Co., Toledo, Ohio, a 1948 graduate of Purdue University.

*George C. Sisler*, Chemical Engineer, Abitibi Research & Development Division, Sault Ste. Marie, Ont., Canada, a 1950 graduate of Queen's University.

*Earl L. Stannard*, Chief Chemist, Stewart Hartshorn Co., Oswego, N. Y., a 1932 graduate of Syracuse University.

*Elgin C. Swackhammer*, Sales Manager, Merchants Chemical Co., Inc., Milwaukee, Wis. Attended Hamilton College.

*Haydn Tanner*, Research Chemist, The Thompson & Norris Mfg. Co. Ltd., Brentwood, Middlesex, England, a 1939 graduate of the University College of Wales.

*Wm. Palmer Taylor*, Research and Development Dept., Champion Paper & Fibre Co., Hamilton, Ohio, a 1923 graduate of the University of Chicago.

*John H. Thresher*, Assistant to the General Manager, National Container Corp. of Wisconsin, Tomahawk, Wis.

*Roy P. Tidman*, Project Engineer, West Virginia Pulp & Paper Co., Covington, Va., a 1947 graduate of Michigan College of Mining and Technology.

*Fred E. Waugh*, Box Plant Manager, Ball Brothers Co., Inc., Muncie, Ind.

*Gustaf W. Wetterling*, Superintendent, AB Klippans Finpappersbruk, Klippan, Sweden, a 1910 graduate of the Technical College, Boras, Sweden.

## *TAPPI Notes*

*Edward S. Atkinson*, formerly student at Tulane University, is now a chemical engineer with the Buckeye Cotton Oil Co., Memphis, Tenn.

*Seward N. Bazler*, formerly of the Mead Corp., Kingsport, Tenn., is now a student at Ohio State University, Columbus, Ohio.

*Benno J. Beau*, formerly with the National Container Corp. of Wisconsin, is now Chemical Engineer for the Jaite Co., Jaite, Ohio, a division of the National Container Corp.

*Lester J. Beaulieu*, formerly of the American Coating Mills, is now Technical Director of the Sherman Paper Products Co., Newton Upper Falls, Mass.

*Otto Berberich*, of the International Printing Ink Co. has been transferred from the New York City laboratory to the plant in Elizabeth, N. J.

*Albert H. Borchardt* is now Vice-President of the Worthington Pump & Machinery Co., Harrison, N. J.

*James P. Casey*, formerly Professor at the New York State College of Forestry, is now Director of Technical Service, A. E. Staley Mfg. Co., Decatur, Ill.

*Robert R. Davis* is now Assistant Technologist, Sinclair Research Laboratories, Inc., Harvey, Ill.

*Francis P. Desmond*, formerly of the Merrimac Paper Co., is now Technical Representative, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

*Francis P. Gallagher*, formerly student at the New York State College of Forestry, is now Trainee with the Hammermill Paper Co., Erie, Pa.

*Alfred T. Gardner* is now Manager of Provincial Paper Ltd., Thorold, Ont., Canada.

*Vincent de P. Gerbereux* is now Manager of the Centrifugal Pump Div., Worthington Pump & Machinery Co., Harrison, N. J.

*Alfred M. Heald*, formerly of the Marathon Corp., is now Research Chemist for the Scott Paper Co., Chester, Pa.

*Robert E. Ingison*, formerly of the Champion Paper & Fibre Co., is now Mill Chemist for the Aetna Paper Co., Div., Howard Paper Mills, Inc., Dayton, Ohio.

*Nard Jones*, formerly of *Pulp and Paper Magazine*, is now a Writing Consultant, 450 E. 63rd St., New York, N. Y.

*A. A. Luce*, of the Torrington Co. has been transferred from the Boston to the Rochester, N. Y., office of the Company.

*Leslie G. McGowan* is now Technical Assistant to the Superintendent, Sorg Paper Co., Middletown, Ohio.

*Donald C. Morris*, Plant Engineer of the Armstrong Cork Co., has been transferred from Pensacola, Fla., to Lancaster, Pa.

*Louis L. Mrachek* is now Construction Superintendent, the Mead Corp., Kingsport, Tenn.

*Robert A. Negaard*, Chemist for the Paper Div., Continental Can Co., has been transferred from Utica, N. Y., to Newark, N. J.

*Frank T. Peterson*, formerly of B. C. International, is now Engineer for the Black-Clawson Co., Hamilton, Ohio.

*Henry B. Pratt*, formerly Assistant Chief Construction Engineer for the Union Bag & Paper Corp., is now with the Puget Sound Pulp & Timber Co., Bellingham, Wash.

*William A. Rolke*, formerly of the American Can Co., is now Chemical Engineer in the Research Dept., Commercial Solvents Co., Terre Haute, Ind.

*Paul M. Schaffrath*, formerly of the staff of the New York State College of Forestry, is now in the Research Dept., Oxford Paper Co., Rumford, Me.

*Howard K. Sheldon*, formerly of the Marathon Corp., is now Assistant Nitrocellulose Superintendent with the Liberty Powder Defense Corp., Baraboo, Wis.

*James B. Sisson* of the St. Regis Paper Co., Oswego, N. Y., is now Chemist for the Polyethylene Coating Dept. of the Company at Carthage, N. Y.

*Edward J. Sullivan* is now Chief of the Fine and Printing Paper Section, Pulp, Paper and Paperboard Div.. N.P.A., Dept. of Commerce, Washington 25, D. C.

*W. H. Swanson* is now Director of Manufacturing, Kimberly-Clark Corp., Neenah, Wis.

*Joseph F. Theriault*, Chemist of the Robert Gair Co., has been transferred from Haverhill, Mass., to Uncasville, Conn.

*Bernard J. Twisdale* is now Chief Chemist for the National Paper Corp., Ransom, Pa.

*Frederick M. Viles*, formerly of American Aniline Products, Inc., is now in charge of Instrument Design, Barkley & Dexter Laboratories, Inc., Boston, Mass.

*Norval F. Wilson*, formerly of the Alton Box Board Co., is now Chief Chemist for the Missisquoi Corp., Sheldon Springs, Vt.

*Hsiao-Ching Yang*, formerly of the Kleen-Fibre Corp., is now Research Chemist for Crown Zellerbach Corp., Camas, Wash.

* * *

L. S. Johnson, official corporate representative of the Cornell Paperboard Products Co., has moved his office from Cornell, Wis., to 1514 E. Thomas Ave., Milwaukee, Wis.

Pierre Franchet, Manager of the Paper Mill of S. A. des Anciens Ets. Braunstein Frères, Paris, France, has succeeded R. Braunstein (deceased) as the official corporate representative of the Company in TAPPI.

* * *

The Columbia Chemical Div. of the Pittsburgh Plate Glass Co. and the Southern Alkali Corp. will hereafter be known as the Columbia-Southern Chemical Corp., a subsidiary of the Pittsburgh Plate Glass Co.

Clyde E. Cromwell, Sales Manager of the Commercial Div. of the De Laval Steam Turbine Co., Trenton, N. J,. has succeeded John W. Hall as the official representative of the Company in TAPPI.

Harold S. Dahlberg, Laboratory Director of F. C. Huyck & Sons, Rensselaer, N. Y., has succeeded E. A. Reese (retired) as the official representative of his company in TAPPI.

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✓ **Detailed knowledge of paper making . . .**
the result of a long and close association with the industry. SOLVAY has served the paper industry longer than any other alkali manufacturer!

✓ **Quality paper-making chemicals . . .**
dependable quality that assures you of chemical materials to meet your production specifications.

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not just specialists in alkalies, but experts in paper-making! SOLVAY Technical Service is at your service—to help solve production problems; and to help prevent them.

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a nationwide group of supply points (backed by three manufacturing plants) that reduces the delivery problem to a minimum, keeps your production running smoothly.

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**LIQUID CHLORINE**
**CAUSTIC SODA**
**SODA ASH**

Soda Ash • Caustic Soda • Caustic Potash • Chlorine • Potassium Carbonate • Calcium Chloride • Sodium Bicarbonate • Specialty Cleansers • Sodium Nitrite
Nytron • Ammonium Bicarbonate • Para-dichlorobenzene • Ortho-dichlorobenzene • Monochlorobenzene • Methanol • Ammonium Chloride • Formaldehyde

## *Industry Notes*

According to the *Chemical Week* eleven expansion projects will boost daily output of semichemical pulp from its present 2500 tons to 3500 tons. This will be a four-fold increase over a 5-year period.

* * *

Sulphur supplies have caused anxiety for over 100 years. The early British chemical manufacturers used Sicilian brimstone exclusively and were disturbed when, in 1838, the king of Sicily granted a marketing monopoly to a French concern, with the result that prices were boosted alarmingly. As a result, in 1839, there were eighteen patents for pyrites burning processes filed in Britain. Pyrites continued to be used until 1860 when the Herman Frasch process of steam extraction was developed and applied in the United States. This process which produced sulphur at unheard of low prices was first commercially operated by the Union Sulphur Co., who in 1903 extracted 190,000 tons in its first year of operation. By 1914 it had reached a production of 418,000 tons, compared with 370,000 tons in Sicily. In 1918 some 1,350,000 tons were extracted in the Gulf area and thenceforth the Sicilian industry steadily declined in the face of American competition.

* * *

The new sulphur deposits discovered in Louisiana by the Texas Co. and to be mined by the Freeport Sulphur Co. will, when developed by 1953, add about 500,000 long tons to the nation's supply. These new deposits are said to be the largest single sulphur mining project developed anywhere in the world in twenty years.

* * *

The setting up of facilities for the extraction of sulphur from Spanish pyrites in the Toulouse region, together with an increase in output from the deposits of Languedoc and Provence, should enable France to balance her sulphur needs and resources by 1953.

* * *

High-frequency sound can now be utilized in full-scale processing equipment to speed up such reactions as distillation, extraction, polymerization, oxidation, coagulation, and the like. Hitherto the use of so-called ultrasonic energy has been limited in capacity to the test tube and laboratory stage.

The chief function of the ultrasonic energy is to subject chemical reaction to what might be considered "terrific shaking." The vibrations set up by the ultrasonic generator reach a frequency of one million per second. As a result, reactions which normally require several hours to complete might be accomplished in a matter of minutes or even seconds.

The prime source of ultrasonic force is found in so-called piezoelectric devices. Quartz and similar crystals have such properties. This means that their crystalline structure produces controlled vibrations on the application of electric current. Quartz is scarce material and particularly expensive in the large shapes required for industrial-scale use of ultrasonics.

A new ceramic has been developed which has a low impedance in comparison with quartz. This means that a very low voltage can produce the same acoustical energy that would require a very high voltage for quartz. Quartz-type generators, for example, necessitate an input of 2000 volts or more, whereas ceramic elements will operate satisfactorily in the range of 50 to 100 volts.

As yet, many chemical engineering requirements in the field of ultrasonics have not been met. The chief problems, in addition to the proper size of the generator, include discovering the best operating conditions, designing accessory equipment, determining methods and techniques to be employed, and circulating the existing knowledge of the subject.

The output of polyethylene should be increased by 40% over 1950 and by 120% by the end of 1952 due to the expansions of Du Pont and Bakelite, the two principal producers. The present production is about 55 million pounds annually. The N.P.A. estimates for the end-uses of polyethylene as of July, 1951 are: military—45.8%; nonpackaging—27.2%; packaging—12.9%; closeness—1.6%; and unrestricted—12.5%. The raw material ethylene is abundant and cheap. Polyethylene has a combination of properties that is possibly unique among the plastics materials: low-temperature flexibility, resistance to oxidation and solvent action, strong transparent films, good insulating properties, and water resistance. These versatile properties have brought polyethylene into prominence for uses in coating papers, fabrics, and metals. Under more normal economic conditions polyethylene may be a serious challenge to the glass container industry and will compete favorably with vinyl plastics and with cellophane for the film market.

* * *

Three million home freezers are now in use. Two hundred thousand retail stores are equipped with over 100 million dollars worth of freezing cabinets according to G. L. Mentley, Sales Manager of Birdseye Div., General Foods Co. Thirty-two thousand insulated railway cars and trucks are in use for transporting frozen foods. There are 11,000 quick-freezing lockers. The per capita consumption of frozen foods increased from 1.6 pounds in 1939 to 10 in 1950. The paper industry is playing an important role in the packaging of quick-frozen foods.

* * *

Paul Schoen, at present Secretary of the Forest Farmers Assn., Valdosta, Ga., has succeeded Fred Morrell in charge of the Washington, D. C., office of the American Paper & Pulp Assn.

* * *

Four companies: Walden Sons & Mott, Inc., Missisquoi Corp., Martin Cantine Co., and Paper Sales Co., formerly of 41 Park Row, New York, N. Y., have found office space at 93 Worth St., New York, N. Y., and will move in October. 41 Park Row has been the headquarters for 40 paper companies' sales departments. Until 1905 the building was occupied by the New York *Times*. The property was sold recently to Pace College.

* * *

In the top 100 national newspaper advertisers in 1950, Scott Paper Co. ranked 95th. There were no other paper manufacturers included in the first 100, although Johnson & Johnson Co., who make paper and a number of paper products ranked 77th.

* * *

The per capita consumption of paper in pounds, as worked out by the American Paper and Pulp Association from census figures, is as follows:

| | 1899 | 1925 | 1950 |
|---|---|---|---|
| All grades | 57.9 | 179.8 | 381.2 |
| Paperboard | 10.5 | 57.0 | 160.0 |
| All paper | 47.4 | 122.8 | 221.2 |
| Newsprint | 15.2 | 51.6 | 76.8 |
| Book papers | 8.1 | 20.0 | 43.4 |
| Fine papers | 3.5 | 8.6 | 15.6 |
| Coarse papers | 14.3 | 22.2 | 43.8 |
| Tissue | 0.8 | 4.8 | 17.6 |
| All other grades | 5.5 | 15.6 | 24.0 |

The apparent per capita consumption of paper for 1951, in spite of a large gain in population, is 414.6 pounds. This is an all-time high.

# HERMANN *Improved* CLAFLIN

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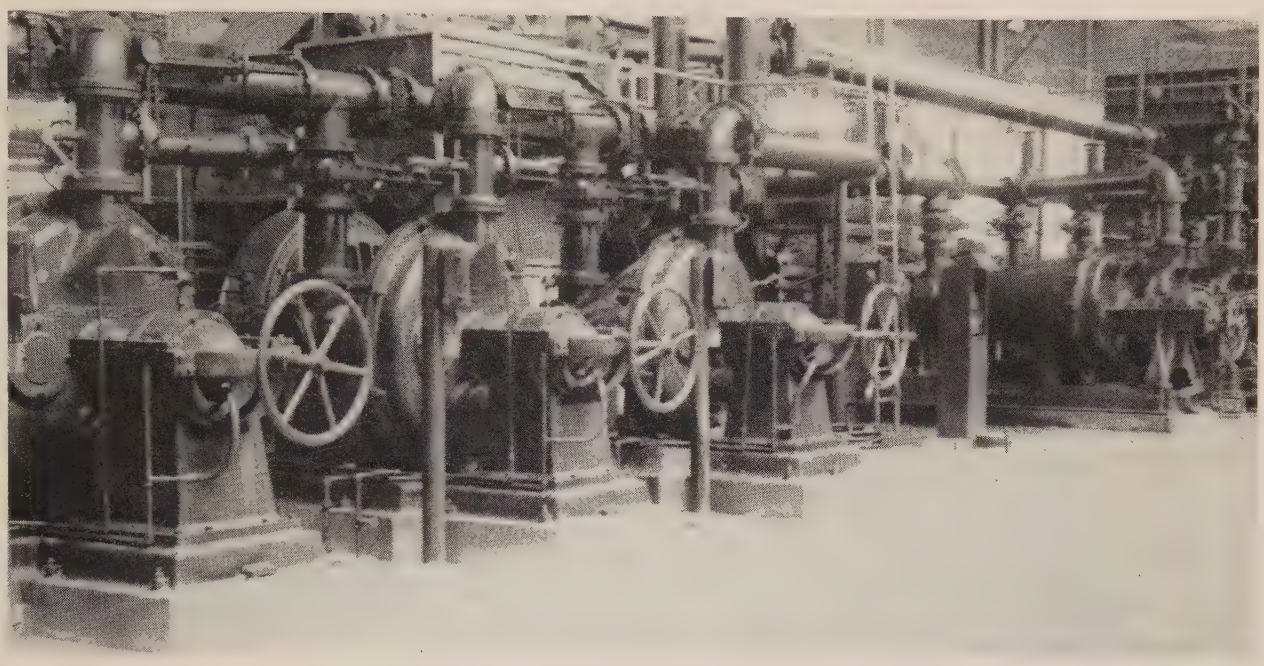
## CONTINUOUS BEATING



THREE LARGE No. 3 HERMANN CLAFLINS USED FOR BEATING, PRODUCING COMPARABLE RESULTS PREVIOUSLY REQUIRING TEN TO TWELVE BEATERS. PRODUCTION UP TO 260 TONS PER DAY OF HIGH QUALITY BAG PAPER.

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TWO LARGE NORTHERN MILLS NOW HAVE THIRTY-THREE No. 2 HERMANN CLAFLINS AND ONE No. 3 FOR CONTINUOUS BEATING, PREBEATING AND REFINING OPERATIONS.

*LOW INITIAL COST - LOW POWER PER TON - LOW MAINTENANCE*

**Exclusive Sales Agent: THE EMERSON MFG. CO., LAWRENCE, MASS.**

# THE HERMANN MANUFACTURING CO.

**Also: TAPPI Standard Pulp Testing-Sheet Making Apparatus**

## LANCASTER, OHIO

The total receipts of pulpwood for the first half of 1951 amounted to 12,304,000 cords, an increase of 35% over the first half of last year. Domestic receipts were 11,082,000 cords and imports 1,222,000 cords. Regionally, the northeast showed a decrease of 17%. The increase in the south was 103%.

Wood pulp production for the first six months of 1951 totaled 8,352,000 tons, a 17% increase over the same period in 1950.

For the first six months of 1951 waste paper receipts averaged 876,000 tons a month in comparison with 610,000 tons in the first half of 1950.

* * *

Plans for Bergstrom Paper Co.'s new waste disposal plant have been completed and forwarded for approval to the stream pollution committee of the state board of health and the state industrial commission. Announcement was made by N. H. Bergstrom, company president.

Applications for necessary steel priorities for the $120,000 building have already been placed with the National Production Authority in anticipation of approval by the state agency. Some pieces of new disposal plant equipment valued at $75,000 and ordered several months ago have been received.

Mill waste treated by the new plant will be used to fill a swampy portion of Little Lake Butte des Morts which was deeded by act of state legislature to the city of Neenah in February. Of the 32 acres of submerged land, slightly over 3 acres were leased by the city on May 16 to Bergstrom Paper Co.

The new waste treatment building will be located 75 feet west of the Soo Line Railroad track which runs behind the mill, in the center of an area 100 feet wide by 100 feet deep allowing room for possible future expansion. Permission has been granted by the Soo Line Railroad to construct a tunnel between the mill and the proposed plant.

The disposal plant building, constructed of structural steel, reinforced concrete framing, and concrete block, will be approximately 100 feet long, 40 feet wide, and 35 feet high. Plant equipment will include a settling tank 64 feet long, 20 feet wide, and 12 feet high, and three storage tanks, each 17 feet 6 inches square and 35 feet high. An operating floor above the settling tank will support the filter and auxiliary equipment.

Early this year, spokesmen for the Neenah-Menasha sewerage commission told state committees that the proposed Bergstrom plant could save the Twin Cities construction of additional sewage disposal facilities which would cost a million and a half dollars. In addition the cities would save $45,000 annually if the company's clay waste could be dumped. Other wastes are burned after treatment in city disposal plants.

The 700,000 gallons of water discharged by the Bergstrom mill each day contain about one-half pound of the settleable suspended waste particles for each 100 pounds of water. Therefore the waste disposal problem begins with separating the fine particles from as much of the water as possible so that the final sludge can be disposed of with ordinary hauling equipment.

Pilot disposal plants have been operated at Bergstrom Paper Co. for several years. The plan finally adopted consists of passing the waste water through settling tanks and later through a vacuum filter. The discharge, a substance of the consistency of putty, is composed of about one pound of solids to two of water. The new disposal plant will supply about 40 to 50 tons of wet fill daily to the 3 acres of submerged land.

Bergstrom Paper Co. will build a retaining wall around the leased property, and the city of Neenah will provide materials for a dyke of rubble to enclose the remainder of the recently acquired area. Depending upon the height finally decided upon by the city, it may take 20 to 30 years to fill the deeded section of lake.

* * *

A large-scale project is now getting underway in Hawaii which will involve a comprehensive study of the possibilities of utilization of sugar cane bagasse. This project is sponsored by the Hawaiian Sugar Planters' Assn., and other interests in their efforts to strengthen Hawaii's economy with new industries. All-out effort will be made to develop the fullest commercial use of bagasse for pulp, paper, feed, and other products.

*George W. Aljian and Joseph E. Atchison*

A group of experts from the pulp and paper industry has joined with the sugar industry experts on this project which may well link the two industries together in the Islands.

It has been announced that the over-all coordinator of this important project will be George W. Aljian, Director of Purchasing and Packaging, California and Hawaiian Sugar Refinery Corp. Mr. Aljian has had some 32 years of experience in the technical and economic phases of the sugar industry. In addition, his extensive work in the field of packaging has made him well known to the U. S. paper industry. During World War II he served as an expert packaging consultant with the Navy and the War Production Board.

Joseph E. Atchison and Elbert C. Lathrop, other key members of this team, are both well known in the pulp and paper industry and both have done extensive work in the field of utilization of agricultural residues.

Dr. Atchison is participating in this project while on a short leave of absence from his position as Chief of the Pulp and Paper Branch of ECA. He is now in Hawaii assisting Mr. Aljian and the sugar industry in preparation of a master plan for the comprehensive study to be made over the next few years on the possibilities of better commercial utilization of bagasse.

The prime movers of this entire program to develop by-products from bagasse have been Leonard D. Baver, Director of the HSPA Experiment Station, and Frederick Simpich, Jr., Secretary of Castle & Cooke, Ltd., and Chairman of the By-Products Committee of HSPA. These men have both worked energetically during the past months to get the project set up and in position to go forward.

The team of Aljian, Atchison, and Baver is now hard at work on the master plan to be followed in the investigations. Fulfillment of this plan may, however, require years of intensive effort, although some phases may be dropped from time to time because of established economic or technical obstacles under present-day conditions.

# SULPHUR

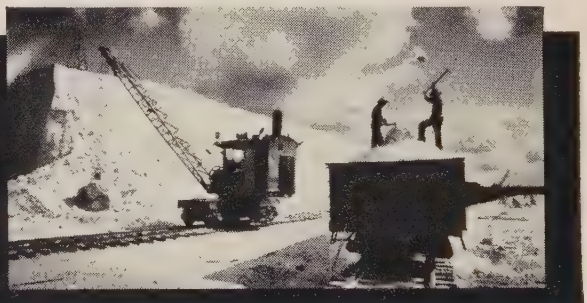
*Interesting Facts Concerning This Basic Raw Material from the Gulf Coast Region

## *MOLTEN SULPHUR

The discharge lines from the wells deliver the sulphur into sumps at collecting stations which are located near the area being "steamed."

The sump is dimensioned to suit operating conditions, as well as the number of wells supplying sulphur. Cast iron has been found the most suitable material for lining the sump, and for the steam coils on the bottom and at the sides which keep the sulphur in a liquid state. When the sump is reasonably full, pumps force the liquid sulphur through insulated pipe lines to the vats. The pumps are especially designed for this service, the moving parts being either submerged in liquid sulphur or steam-jacketed.

Loading operations at our Newgulf, Texas' mine



TEXAS GULF SULPHUR CO. INC.

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Mines: Newgulf and Moss Bluff, Texas

As a result of this preliminary study of the problems involved and as work progresses on specific phases of the project, the services of other available experts in this field will be utilized. It may also be desirable to utilize the facilities of other research laboratories, semicommercial and commercial plants as the work progresses.

Several separate and distinct phases of activities seem imminent in this study. In general, these are as follows:

1. Developing the most efficient method of separation of pith from fiber so that each fraction can be recovered in suitable condition for commercial utilization. No large-scale commercial process has yet been put in operation which satisfies these requirements, yet the future development of the entire project depends upon successful separation of pith and fiber. A small-scale pilot plant for separation of pith and fiber is now in operation at the Peoria laboratory and a large scale semicommercial unit is in operation at Oahu Sugar Co. in Hawaii. Although the results thus far have been promising, a tremendous amount of work remains to be done on this problem before a successful commercial operation can be assured. Work on this phase will be intensified during the next year.

2. Developing suitable uses for the pith fraction. At the present time the most promising use appears to be in the field of livestock feed for which there is a ready market in the Islands. Intensive work will be done toward determining the most suitable mixture of pith, molasses, protein, and other ingredients necessary for livestock feed. Work in Hawaii involves close collaboration with the University of Hawaii and with local ranchers.

3. Determining the suitability of the fiber for utilization in the pulp and paper industry. This is a broad field and has many possibilities, all of which will be included in the study. It will certainly involve a technical and economic study to determine the possibility of establishing a fiber, pulp and/or paper industry in Hawaii. Possible products may include pith-free fiber, corrugating medium, test liner board, mulch paper, building paper, chipboard, bleached pulp, bleached paper and paperboard, etc.

4. Determining the possibilities of manufacturing chemicals from molasses and bagasse, and possibilities of manufacturing in the Islands those chemicals required in pulp and paper manufacture.

* * *

Assuring a sufficient flow of pulpwood to the mills is a major problem of the pulp and paper industry in Norway. Considerations of conservation and lack of manpower have made it impractical to increase the timber cut by any substantial amount. In 1950 chemical pulp export to the United States amounted to 26,000 tons. Further expansion of Norway's industry has been discouraged by the government. The latter requires that a mill purchasing new machinery must either scrap the old or otherwise render it unusable so as to prevent further expansion of processing capacity.

* * *

An APPA translation from *Das Papier* (July 30, 1951) it is reported that Russian paper and board production has increased 47% over 1940 (State Planning Administration and Central Statistical Administration of the USSR). In this last prewar year, production was about 810,000 metric tons, and in 1950, on a comparative basis, 1,190,700 tons were produced. The plan had called for a production of 1,224,000 metric tons for 1950, of which Russia proper was to supply 81.4%, Finnish Karelia 11.6%, Estonia and Latvia each 2.8%, and Lithuania 1.4%.

In the past year Russian production on a comparative basis surpassed Sweden's (about 1,170,000 tons in 1950). Russian production was also equal to 76% of West Germany's paper and board production. The per capita consumption in the Soviet Union in 1950 was 13.2 pounds (using as a base a countable population of 200 million).

The development of Russian production of paper and board since 1913 is shown in the following tonnage figures: 1913—197,000; 1929—385,000; 1937—832,000; 1940—810,000; 1945—333,000; 1946—536,130; 1947—723,000; 1948—857,000; 1949—899,110; and 1950—1,190,700 tons.

* * *

N. P. A. Order M-27, Direction 1, establishes a formula, where a consumer of Northern European pulp is permitted to increase his over-all inventories of market chemical pulp during the winter months in direct proportion to his relative dependence upon European pulp. The maximum allowable inventory is 120 days. After June 1, 1952, inventories will revert back to a 45-day limit on all market chemical wood pulp, as provided in Section 4 of N.P.A. Order No. M-72.

* * *

The total population of the United States, including armed forces overseas, was about 154,353,000, as of July 1, 1951. This figure represents an increase of 3,221,000 or 2.1% over the corresponding estimate for April 1, 1950.

* * *

N.P.A. Order M-71, as amended Aug. 23, 1951, provides priorities assistance to technical and scientific laboratories. This revised regulation makes clear that production control laboratories may use the order. The priorities relate to steel, copper, and aluminum needed by the laboratories.

* * *

Conservative estimates place Alaska's coastal and interior forest lands at more than 375,000 square miles or almost twice as large as the combined forest lands of the four Scandinavian countries where forest industries are a major factor in the economy.

Alaska's most productive forest region is the 16 million-acre Tongass National Forest in southeastern Alaska, where some 5 million acres have been classified as merchantable timber. At least 75% of this timber stands within 2½ miles of tidewater, and is predominantly hemlock and spruce.

The interior forests of Alaska are composed mainly of white spruce and birch and covers an estimate 342,000-square mile area along the Yukon, Tanana, Kuskowin, and Copper Rivers. A rough estimate places the volume of these interior forests at 910 million cords.

Preliminary investigations indicate that there is sufficient timber and waterpower now available to supply five or six pulp and paper mills of 500-ton daily capacity.

* * *

Certificates of necessity issued since July include the following:

| | | |
|---|---|---|
| Brown Co. | $3,151,876 | 65% eligible |
| Penobscot Chem. Fibre Co. | 817,717 | 65% eligible |
| Fitchburg Paper Co. | 208,409 | 65% eligible |
| West Va. Pulp & Paper Co. | 3,500,000 | 65% eligible |
| Mosinee Paper Mills | 700,000 | 60% eligible |
| Fibreboard Products, Inc. | 1,439,404 | 50% eligible |
| Ketchikan Pulp & Paper Co. | 36,663,500 | 65% eligible |
| Crossett Lumber Co. | 93,255 | 50% eligible |

* * *

The U. S. Customs Court has supported the position of the Import Committee of the Paper Industry that paper containing over 6½% ash is not duty free as standard newsprint, but dutiable as printing paper. The case involved 30 separate shipments of paper with ash ranging from 7½ to 15%, according to Warren B. Bullock, Manager of the Committee.

* * *

The percentage increase of industrial production for the ten leading manufacturers for the first half of 1951 over the same 1950 period are: machinery—35; transportation equip-

# Industry's Modern Shield of PROTECTION

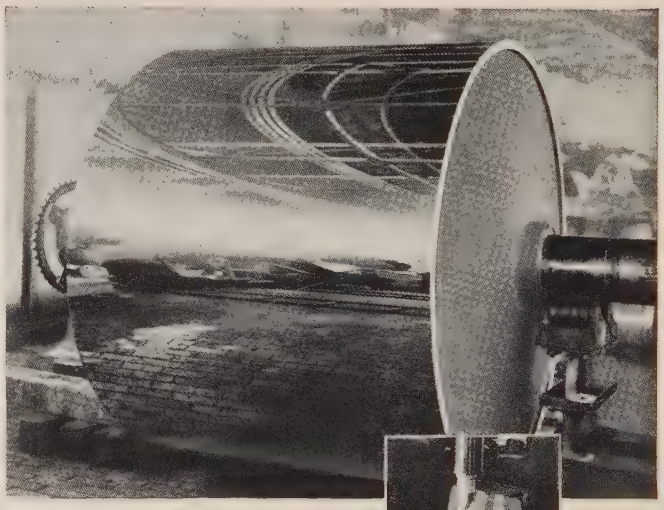
CRODON
The Chrome Plate
TRADE MARK REG. U.S. PAT. OFF.

*Industrial chromium plating provides, protects and preserves flawless, precision-finished surfaces where protection against wear and corrosion is vital.*

Long after ordinary equipment has been discarded, chromium-plated parts continue in regular operation. Protection against wear and corrosion does more than simply prolong useful life . . . it maintains new-equipment efficiency for extended periods. This unusual performance assures drastically reduced costs, coupled with increased operating efficiency and improved quality of product.

Chromium is the hardest commercial metal. Industrial CRODON-plating greatly prolongs equipment life and provides substantial operating economies. CRODON-plated equipment guarantees a better product. New-equipment performance is maintained for extended periods. Freedom from product contamination and attainment of more perfect finishes are substantial advantages. The normal life of parts is prolonged by chromium plating. Equipment replacement is less frequent. Maintenance expense and operating delays are reduced. The consistently satisfactory performance of CRODON-plated equipment also provides many other economies.

The trade-mark CRODON assures the best in chromium plating. CRODON is the dependable guarantee of the most practicable and economical service available. Behind every CRODON application are the resources, experience and reputation of America's oldest and largest industrial chromium plating organization.



*Surface protection, long wear and a better finished product result from this high-lustre CRODON-plated 6-ton steel drum, 6' diameter x 5' face.*

*Chromium plating of small tools and parts is practical, inexpensive and provides many operating benefits.*

*Write for further information.*

CRODON PLATING pays

## Chromium Corporation of America

**Executive Offices: 100 East 42nd Street, New York 17, N. Y.**

346 Huntingdon Ave.
Waterbury 90, Conn.

1760 Lakeview Road
Cleveland 12, Ohio

4645 West Chicago Ave.
Chicago 51, Ill.

ment—28; stone, clay, and glass products—21; iron and steel—21; chemicals—17; paper and products—16; textiles—8; lumber—8; printing and publishing—5; and manufactured food products—2.

* * *

Printing plates made of rubber are helping J. W. Clement Co. of Buffalo to preserve storage space. Clement is one of the few large-edition commercial printers in the country using rubber plates, developed after World War II. The rubber plates, called running plates are less than $^1/_2$ inch thick and weigh much less than the metal plates formerly used. The plates are used only for straight letterpress printing, such as pocket-size novels.

Paper, with an adhesive on both sides, is used to apply the rubber plates to the press. They can be removed faster than metal plates. It is only since the development of synthetic rubber that the printing industry has been able to use rubber to make running plates because the synthetic is impervious to oils and chemicals in the ink. The rubber plates are claimed by Clement to be more efficient and durable than the metal units and never seem to wear out. Clement makes its own rubber plates. It gets rubber in sheets. These are cut to size and the imprint is pressed into the rubber under heat from a plastic mold. These molds are made of the original engravings or newly set type.

* * *

To aid the economic development of Turkey, the government has invited a group of Turkish engineers, including four employed in the pulp and paper industry to study industrial management at the New York School of Industrial and Labor Relations at Cornell University. There will be two months of classroom training and three months of in-plant training.

* * *

The N.P.A. Industry Advisory Committee for the Corrugated and Solid Fiber Shipping Container Industry is as follows:

Burritt S. Hubbard, Ashtabula Corrugated Box Co.
J. V. Spachner, Container Corp. of America.
L. H. Schroeder, Dixie Container Corp.
Charles W. Evert, Downing Box Co.
B. P. Altick, Fibreboard Products, Inc.
H. M. Treen, Fort Wayne Corrugated Paper Co.
George E. Dyke, Robert Gair Co.
J. M. Arndt, Gaylord Container Co.
David H. Rous, Grand City Container Corp.
Shelley Schuster, Great Southern Box Co.
Sidney Frohman, Hinde & Dauch Paper Co.
W. S. Snyder, International Paper Co.
C. H. Carpenter, Kiechhefer Container Co.
J. D. Northrup, Owens-Illinois Glass Co.
J. W. Schiffenhaus, Schiffenhaus Brothers

* * *

The Exposition of Chemical Industries will be held at the Grand Central Palace on Nov. 26 to Dec. 1, 1951.

* * *

The State Forestry Commission of Georgia has been authorized to add $20,000 annually to its appropriation for the Herty Foundation Laboratory in Savannah, Ga. The money will be used for research work with scrub oak and other hardwoods and to find uses for Georgia pine waste.

* * *

The Ohio Boxboard Co., Rittman, Ohio, has appointed Arthur B. Hall to Director of Industrial and Public Relations. Mr. Hall was Vice-President of Personnel and Industrial Engineering for Stahl-Meyer, Inc., New York City, prior to joining Ohio Boxboard Co.

* * *

A new 16-page booklet explaining the development of papermaking is now being distributed by American Forest Products Industries, 1319 18th St., N. W., Washington, D. C. The booklet features a flow chart which shows the papermaking process from the woods to the finished product.

* * *

The Consolidated Water Power and Paper Co. has announced that all sulphite pulp made at its Wisconsin Rapids mill will be manufactured by the ammonium-base sulphite process, instead of by the calcium-base process. The shift is considered as experimental and is expected to continue for several weeks. The current tryout is intended to teach Consolidated the economics of ammonium-base pulping. Previous trial runs indicated that higher costs of digester maintenance are one expectable result.

* * *

The St. Joe Paper Co., Port St. Joe, Fla., has awarded a contract to Tidewater Construction Co. of Norfolk, Va., as general contractor of its 25 million dollar expansion. The work is to start immediately and be concluded by September, 1952, and will increase daily output of kraft paper from 400 to 1200 tons.

* * *

Hendley Blackman has been named manager of the engineering association activities for the Westinghouse Electric Corp. He succeeds Frank Thornton, Jr., who recently retired. Mr. Blackman was formerly managing editor of *Electrical World.*

Harold G. Cheney has been appointed sales manager for the Westinghouse Electronic Tube Div., Bloomfield, N. J.

Westinghouse has issued a 30-page booklet on "How to Select Electrical Measuring Instruments." Booklet B-4696 may be obtained from the Westinghouse Electric Corp., Box 2099, Pittsburgh 30, Pa.

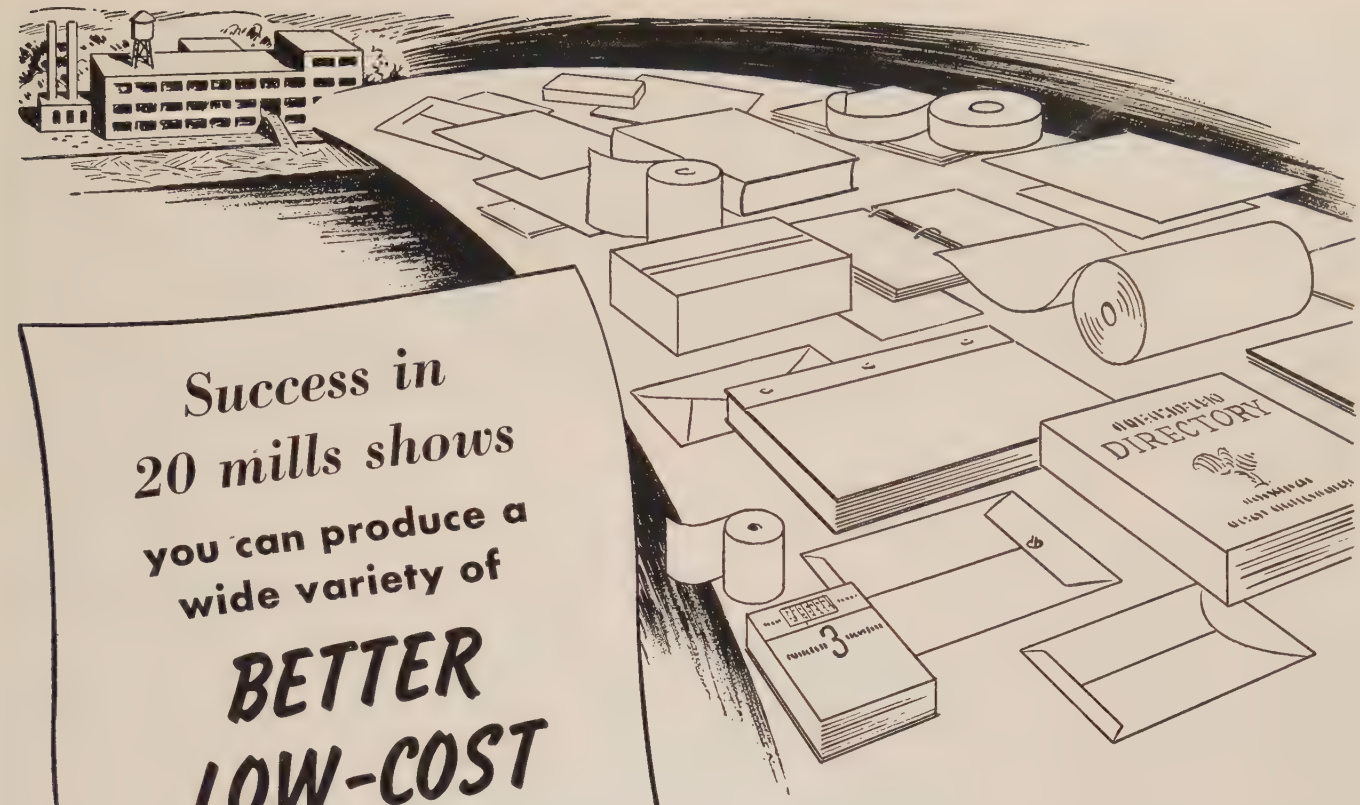
The first application of magnetic amplifiers to the control of a large high-speed winder drive is being made by Westinghouse. They will perform control functions formerly obtained by the use of rotating regulators and, in some cases, electronic equipment. The new winder will handle heavy, 234-inch wide kraft board at operating speeds up to 5000 f.p.m. at a southeastern paper mill. Magnetic amplifiers will provide voltage regulation of the system and current-limit control during acceleration and deceleration of the winder, as well as constant-tension regulation of the breaking generator with provision for inertia compensation. The magnetic amplifier is a static device, consisting of electric coils on an iron core, something like a transformer. It has no bearings, commutator, brushes, or electronic tubes, reducing maintenance to a minimum.

* * *

Three new technical bulletins on Nalco ion exchange materials have been released by the National Aluminate Corp. and are available from the company at 6197 W. 66th Place, Chicago 38, Ill. These bulletins are No. 57 (Nalcite SAR); No. 58 (Nalcite HCR); and No. 59 (Super Nalcolite). Nalcite HCR is a styrene type cation exchanger. Nalcite SAR is a strongly basic anion exchanger and Super Nalcolite is a synthetic gel-type zeolite for cation exchange. Discussions, supplemented with tables and graphs explain the performance of these water-treating resins under various operating conditions.

* * *

M. E. Cody, Vice-President and General Manager of the Black-Clawson Co., Hamilton, Ohio, has announced the appointment of Frank T. Peterson as Assistant to the General Manager of the Hamilton Div., and George M. Pennock as Chief Development Engineer of the Division. Mr. Peterson was formerly Deputy Managing Director of B-C International




## Success in 20 mills shows you can produce a wide variety of BETTER LOW-COST PAPERS

## Plan now for future production with the DU PONT PEROXIDE PULP BLEACHING PROCESSES

Experience in 20 important U. S. and Canadian mills has shown that Du Pont Peroxide Bleaching can enable you to meet the increasing demand for more and better low-cost papers.

And in mill after mill, the advantages of peroxide bleached groundwood have been apparent . . . savings up to 30% in fiber costs . . . improved brightness permitting the use of more bleached groundwood in the furnish . . . both sulfite and groundwood pulps upgraded!

Adaptable for use in bleaching groundwood, sulfite, soda, kraft and semi-chemical pulps, the Du Pont Pulp Bleaching Processes also provide a means of producing higher quality papers from your recovered paper stocks.

**GET THE FACTS FROM DU PONT *today!***

The men who pioneered this modern method of pulp bleaching will be glad to work with you in planning an installation to meet your specific needs. For more information, just clip and mail the coupon below.

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**PEROXIDES**
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**AVAILABLE IN DRUMS AND TANK CARS**
- "Albone" 35 . . . . . Hydrogen Peroxide, 35%
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- "Solozone" . . . . . Sodium Peroxide

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BETTER THINGS FOR BETTER LIVING . . . *THROUGH CHEMISTRY*

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E. I. du Pont de Nemours & Co. (Inc.)
Electrochemicals Dept., Wilmington 98, Delaware

Please send me further information about Du Pont Peroxide Bleaching Processes: (check application)

____Groundwood ____Sulfite ____Soda Pulp ____Kraft
____Semi-chemical pulps ____Waste-paper recovery

*Name*_____
*Position*_____
*Firm*_____
*Address*_____

Ltd. in London and Mr. Pennock was formerly Director of Export Engineering at Middletown, Ohio.

* * *

The new Shartle velocity type cleaning unit for dirty stock, previously known as the Hydraclone, has been changed in name to the Hydrafuge Separator. Its basic application is in the filler stock cleaning system for removing heavy particles. The Shartle Bros. Machine Co., Middletown, Ohio, plans to make name plate changes in over a hundred units now in service.

* * *

Lewis B. Gordon has been appointed Vice-President; Denman Peniston, Director of Sales; and John H. Elleman Assistant Director of Sales of the Solvay Sales Div., Allied Chem. & Dye Corp., New York, N. Y.

* * *

Edward F. Degering, formerly Professor of Chemistry at Purdue University, has joined the staff of Buckman Laboratories, Inc., Memphis, Tenn., as Manager of Research.

* * *

The International Nickel Co., Dept. EZ, New York 5, N. Y., has issued a 28-page booklet on "Guide to the Selection of Engineering Irons." It is compiled principally for design engineers and presents the characteristics of modern nickel cast irons.

* * *

The following appointments have been announced by the American Cyanamid Co.; A. J. Campbell, General Manager of the Industrial Chemicals Division, and Howard Huston, formerly Assistant to the President, have been elected Vice-Presidents. L. C. Duncan was elected Assistant to the President.

Richard F. Warren was named Senior Market Research Analyst of the Market Research Section, New Development Dept. Mr. Warren was formerly Market Editor of *Chemical Engineering Magazine*. A. J. Weith was appointed production supervisor in the Synthetic Organic Chemicals Dept.

* * *

Spencer Chemical Co., Kansas City, Mo., will soon begin the construction of a new anhydrous ammonia plant near Vicksburg, Miss. The cost is estimated at 14 million dollars and is Spencer's fifth unit.

* * *

Technical data on tubing for the pulp and paper industry are presented in a new 8-page illustrated bulletin (TA 1559) issued by Babcock & Wilcox Tube Co., Beaver Falls, Pa.

* * *

Rice Barton Corp., Worcester 1, Mass., is now issuing a monthly publication called the *Cellu-Letter* which deals with current developments. The *High-Road* will continue to be published each month. *The Cellu-Letter* is edited by Nard Jones, formerly of *Pulp and Paper*.

* * *

John P. Schwede, Director of Exports for the Union Bag & Paper Corp., has left on an 18-month trip to Central and South America. He will make his headquarters in Costa Rica and plans to visit all of the Latin-American markets for the purpose of developing a long-range export program for Union Bag products.

* * *

Ross Mekeel has been elected a Director of the Cameron Machine Co. He was purchasing agent for over 25 years and will continue as Secretary of the Company.

Alexander Fleck Ltd., Ottawa, Canada, who have been manufacturing and selling the Brammer consistency regulator under license from Paper & Industrial Appliances, Inc., New York, N. Y., will hereafter handle under license the Chemi-Pulper, used for producing wallboard, roofing felt, kraft and semichemical pulps, and the Morley continuous pulper used for continuous production of pulp from cereal straws, bagasse, and similar materials used in making nine-point board.

* * *

Link Belt Co., 307 N. Michigan Ave., Chicago 1, Ill., has issued a 20-page illustrated booklet (No. 2377) on Model "UP" vibrating screens for dry-screening light and fine materials.

* * *

The Reliance Electric and Engineering Co., 1988 Ivanhoe Rd., Cleveland, Ohio, has appointed four application engineers to its organization. These are: Ralph D. Abercrombie, Jr., Buffalo, N. Y.; Rex T. Willard, Atlanta, Ga.; Merle K. Sieber, New York, N. Y.; and Nicholas D. McKay, Detroit, Mich.

* * *

A two-year multimillion dollar program of plant expansion at the Painesville, Ohio, plant of Diamond Alkali Co. has been announced. This will step up the Company's production of chlorine, soda ash, and caustic soda by the electrolytic method.

* * *

Austin L. Hawk has been appointed manager of the Western Sales District of the Manhattan Rubber Div., Raybestos-Manhattan, Inc., 445 Lake Shore Drive, Chicago, Ill. S. V. Hoffman was appointed regional manager at 4651 Pacific Blvd., Los Angeles, Calif.

* * *

Magnuson Products Corp., 50 Court St., Brooklyn 2, N. Y., has issued a new booklet entitled "Permag Cleaning Compounds for Paper Mills."

* * *

Beavin W. Mills has been appointed sales manager for Gairvure cartons in the Robert Gair Co., New York, N. Y.

* * *

The Improved Paper Machinery Co., Nashua, N. H., has issued a 4-page bulletin (J-100) which features a cutaway drawing of a pulp mill building and a flow diagram showing equipment used in a pulp mill.

* * *

Bulletin No. 30 of the Buffalo Electro-Chemical Co., Station B, Buffalo, N. Y., features "Hydrogen Peroxide in the Manufacture of Viscose." It describes the technique of making viscose rayon and explains the role of hydrogen peroxide in aging alkali cellulose and the ripening of viscose.

* * *

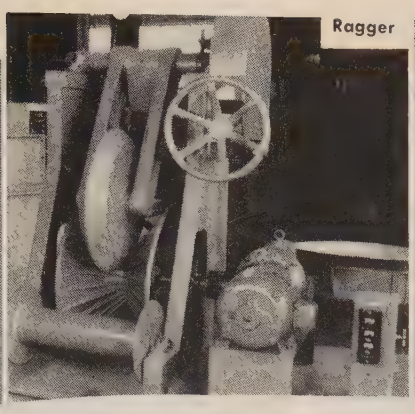
The General Electric Co., Schenectady 5, N. Y., announced a newly designed line of multistage mechanical-drive turbines in ratings of 200–5000 hp. These turbines are used to drive pumps, compressors, fans, blowers, and similar equipment. These are designated DP, DR, DRV and DRUX.

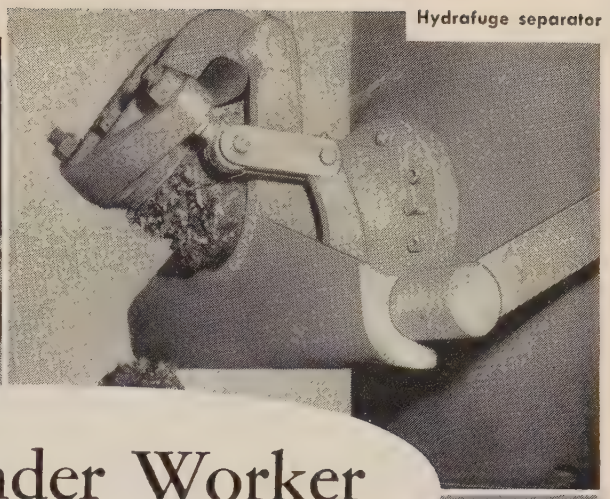
Clifford M. Dunn has been appointed manager of G.E.'s Michigan Apparatus District with headquarters in Detroit.

G.E. has issued a 16-page bulletin (GEA-5521) on Power System Equipment for Pulp and Paper Mills. It features the types of turbine generators now available and points to be considered in making a selection.

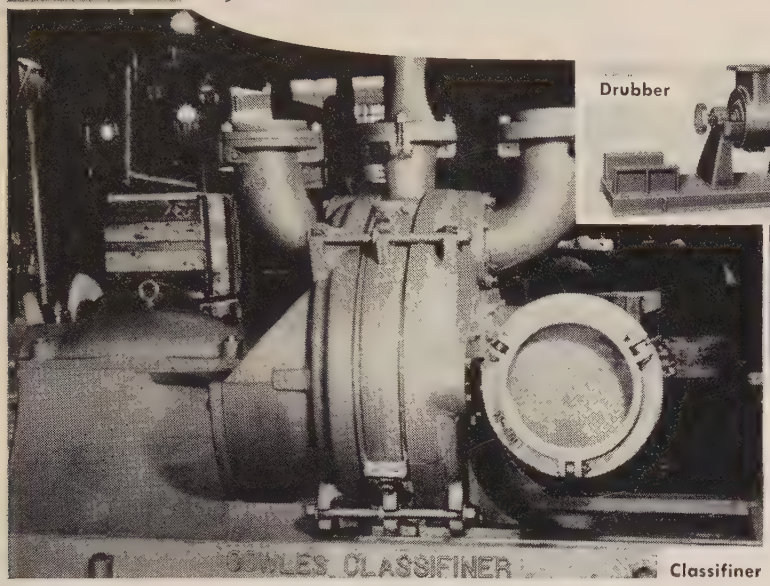
In the first installation of its kind, a G.E. beta-ray gage is being used at the Antioch, Calif., plant of Fibreboard Prod-

Junk remover

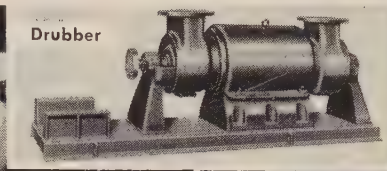

Ragger


Hydrafuge separator

# Board Mill Wonder Worker



Classifiner


Drubber

Selectrap

It stretches the imagination almost to the breaking point to visualize a mechanical "gadget" or system able to take a bale of dirty mixed papers and in almost nothing flat separate the "gold" from the "dross"—paper fiber from all that miscellaneous waste.

That is exactly what a modern Shartle Stock Cleaning System does—making possible the economical use of dirty paper stock and the tremendous expansion of the board division of the Industry.

## How This Board Mill Wonder Worker Works

1. **Junk remover to carry out of the Hydrapulper by bucket conveyor all heavy junk.**
2. **Ragger to reel out baling wires, rags, wet strength and other coarse floating trash.**
3. **Hydrafuge separator to remove all sand, grit, ground glass and other heavier-than-water fine materials.**
4. **Classifiner to screen clips, staples, pins, cork, cellophane, fiber bundles and fiber adhering to clips and staples—passing all free fiber on to thickeners and all rejected material to Disintegrator or Drubber for further salvaging attention.**
5. **Disintegrator, or Drubber, to break loose all fibers still congregated in bundles and all fiber still attached to clips and staples.**
6. **Selectrap to receive all material from Disintegrator or Drubber, separate and salvage any fiber still present and discharge the rejects.**

**There you have it—a Shartle cleaning system at work—salvaging close to 99% of all fiber present in dirty paper stock—truly a Board Mill Wonder Worker.**

## SHARTLE BROTHERS MACHINE COMPANY, MIDDLETOWN, OHIO

DILTS MACHINE WORKS, Fulton, New York
Divisions of THE BLACK-CLAWSON CO., Hamilton, Ohio
Western Sales Office: Mayer Bldg., Portland, Oregon
Southern Sales Office: 937 Coventry Road, Decatur, Georgia

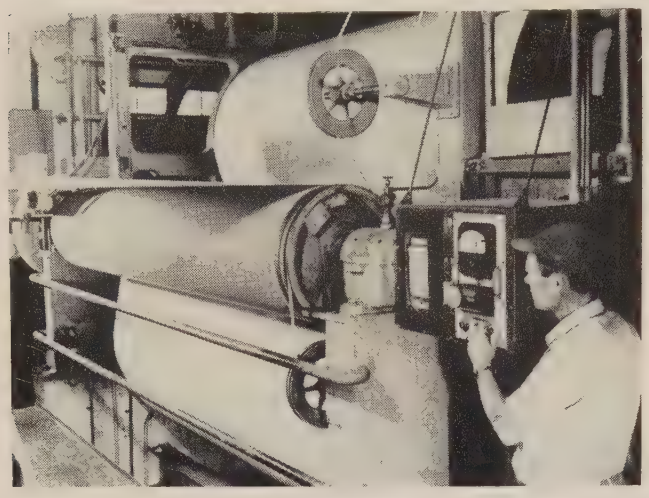
Associate: THE ALEXANDER FLECK LTD., Ottawa, Canada
Subsidiary: B-C INTERNATIONAL, LTD., Greener House, 66/68 Haymarket, London, S. W. 1, England

ucts, Inc., to help maintain accurate and uniform weight of milk carton paperboard.

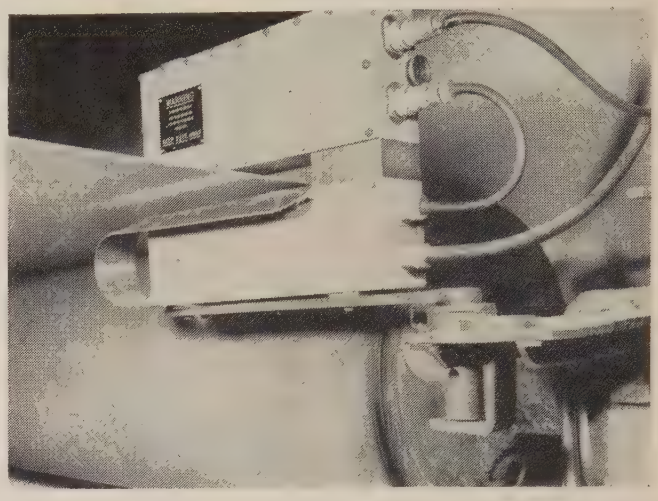
The gage, mounted on one of the company's 136-inch paperboard machines, records the varying amounts of beta-rays absorbed by the board as it passes through the gage head of the noncontacting device. The amount of beta-rays absorbed varies with the weight of the board, thus allowing a constant check to be maintained. Variations as slight as 1% from the desired weight per unit area of the board are automatically indicated and recorded.

Operators are able to make adjustments of the processing machinery as needed to produce paperboard of uniform weight. This is particularly important in the case of milk carton board and similar material that is run through folding machines which operate on extremely close tolerances.

According to E. H. Entricken, in charge of instruments at



*Other side of the machine showing controls, indicator, and continuous recorder*



*Close-up of the gage head installed on the 136-inch paper machine at Fibreboard*

the Fibreboard plant, the G.E. beta-ray gage is "more than a watchdog to prevent bad runs—it also aids in setting up new runs more quickly."

The gage, which is not affected by the speed, consistency, or temperature of the material being measured, may also be applied to plastics, rubber, metals, and special sheet materials where a continuous indication is desired. Since no part of the gage is in actual contact with the material being measured, it leaves no mark or scratch.

* * *

Du Pont has announced that it has developed a new and economical way to add neoprene to paper.

Instead of coating or saturating the finished paper, the neoprene is added in latex form to the pulp just before it is made into paper. The result is a new family of specialty papers made directly on the paper machine. These papers have high wet strength and chemical resistance.

Among the products that can be made of such papers are woven paper rugs. They have high-abrasion resistance and can be washed with soap and water and dried without losing their shape. Double-wall insulated bags for cold bottles or cans use neoprene-treated paper so that the bag will not break when water condenses on the containers. In the industrial field this paper has undergone field trials in such applications as gasket paper, multiwall bag paper, wrapping paper, boxboard, and industrial filter paper. E. I. du Pont de Nemours & Co., Inc., Wilmington 98, Del., advises that it will not manufacture these papers but will sell neoprene and advise paper manufacturers relative to its specific uses.

* * *

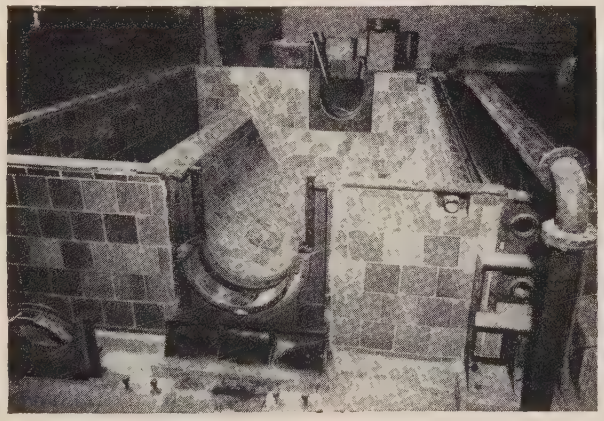
The Heppenstall Co., Boston district sales office, has been removed to Room 808, Statler Office Bldg., 20 Providence St., Boston 16, Mass. A. V. Alderson and George H. Wurster will be located at this new address.

*Making ready to lift truck load of logs for transferring to railroad car*

* * *

The H. W. Butterworth & Sons Co., makers of Butterworth calender rolls, embossing calenders, friction calenders, and special 3-roll calenders for the paper industry, have recently completed a $300,000 expansion at Bethayres, Pa.

The new building, with 68,000 square feet of floor space houses the pressed roll department and includes the most modern machinery for the manufacture of calender rolls for coated stock, super and glassine.



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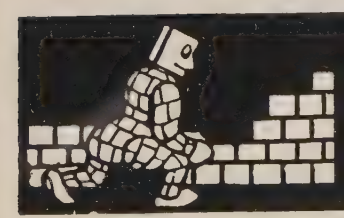
—is extensively used to provide better operation and longer life for vessels, chests, treating or storage tanks used in the pulp and paper industry.

Whenever you have a lining or tank problem consult a Stebbins engineer. This advice is based on experience gained over many years devoted to meeting the needs of pulp and paper mills.

A consultation involves no obligation on your part and may save thousands of dollars in future operating and maintenance costs.



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WATERTOWN, NEW YORK

CANADIAN STEBBINS ENG. & MFG. CO., LTD. — CASTLE BLDG., MONTREAL, CANADA

STEBBINS ENGINEERING CORP. — TEXTILE TOWER, SEATTLE, WASH.

# News by the Mile for Millions

Consider the improved appearance of today's newspapers. Pictures are sharper, type impressions are clearer and easier to read. Better quality finishes have contributed directly to this change.

In every part of the country, paper mills rely on Butterworth Calender Rolls for smoother, better paper finishes at lower costs.

If you are experiencing calendering problems—losing production time or getting inferior finishes, then make this important test. Put a Butterworth Roll in the stack. See and feel the difference in the finish. Check the increased production time—extra hours of top flight service with fewer delays.

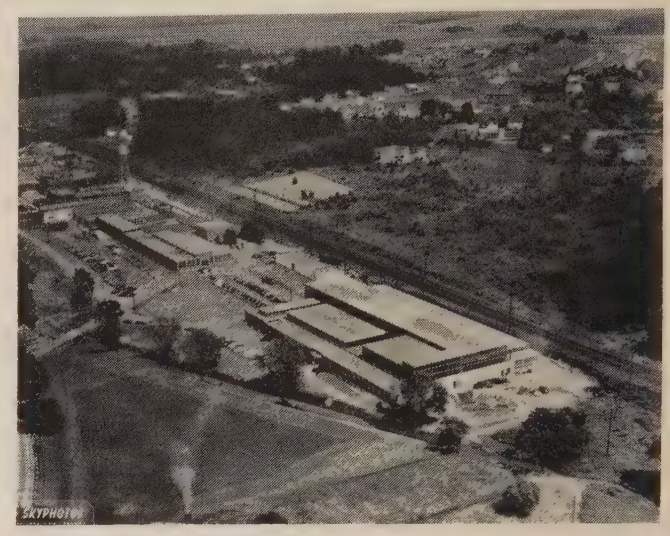
Butterworth Calender Rolls are made of the finest materials available. Built to meet your exact calendering needs and specifications. Your present rolls can also be refilled. Get the facts on better calendering today.

For full information, write or call H. W. Butterworth & Sons Company, Bethayres, Pennsylvania—40 Fountain Street, Providence, R. I. : : 1211 Johnston Building, Charlotte, N. C.

Butterworth
CALENDER ROLLS

The new plant is the third step in a 4-year expansion program. In 1947, Butterworth completed a large new machine shop at Bethayres. In 1950, the firm converted its Bethayres foundry for manufacturing operations.

The present operating capacity is at the highest point in the 130-year history of the company. The improvements made at Bethayres will reduce the time element in production and will speed deliveries.



*Aerial view of H. W. Butterworth & Sons Co. plant, Bethayres, Pa.*

Butterworth has offices in Providence, R. I., and Charlotte, N. C. Harry W. Butterworth, Jr., is President. The other officers include: De Haven Butterworth, Vice-President, J. Ebert Butterworth, Vice-President and Secretary, and John H. S. Spencer, Executive Vice-President and Treasurer.

***Sixth generation of the Butterworth family—nephews of the president—with executives of the firm. L. to r.: J. Ebert Butterworth, Vice-President and Secretary; J. Ebert Butterworth, Jr.; Harry W. Butterworth, Jr., President; DeHaven Butterworth, Vice-President in Charge of Sales; John H. S. Spencer, Executive Vice-President and Treasurer; DeHaven Butterworth, Jr.***

The sixth generation of the Butterworth Family, DeHaven Butterworth, Jr., and John H. S. Spencer, Jr., nephews of the President, are now serving apprenticeship with the firm.

* * *

*Sulphate chip conveyor from sawmills at Longview mill of the Weyerhaeuser Timber Co.*

The De Laval Steam Turbine Co. of Trenton, N. J., has announced the completion of a new building at 160 Folsom St., San Francisco, Calif., to be its new headquarters for local sales and service activites. C. F. Reeves is in charge of De Laval's West Coast sales.

* * *

The Weyerhaeuser Timber Co. will build a new 20 million dollar pulp mill at Everett, Wash. The new plant will produce 250 tons per day of bleached kraft from Douglas-fir sawmill waste.

# OBITUARIES

## John D. Watson

John D. Watson, 71, Vice-President of the Wisconsin Wire Works, died on Aug. 23, 1951, after a long illness.

Mr. Watson was born on Oct. 3, 1879, in Edinburgh, Scotland, and moved to Appleton, Wis., when he was seven years old. He was Manager of the Wisconsin Wire Works since 1904.

He was a member of the Appleton Vocational School Board for 28 years and served as its President for 10 years. At the time of his death he was Director of the Pacific Coast Paper Mills, Bellingham, Wash.

Surviving are two daughters and three sons, a brother, a sister, and three grandchildren. His son James, an engineer with the Wisconsin Wire Works, is a member of the Technical Association of the Pulp and Paper Industry.

## Robert Tait Petrie

Robert T. Petrie was among those who perished in the airplane tragedy near Oakland, Calif., on Friday, August 24.

Mr. Petrie was the Western Sales Manager of the Black-Clawson Co. and had his office in the Mayer Bldg., Portland, Ore. He had returned to the home office at Hamilton and Middletown, Ohio, to attend the general Black-Clawson, Shartle, Dilts sales meeting and had traveled with the sales group to Fulton, N. Y., for further meetings with the Dilts Machine Works Division.

*Robert T. Petrie*

Mr. Petrie was born in the Shetland Islands, Scotland, on Sept. 17, 1897. Prior to joining Black-Clawson he had been employed by the Canadian National Railways, Canadian Power & Light Co., Glenburn Finclay and Pottery Co. (New Zealand), Price Bros. Co., The Minton Vacuum Dryer Co., and the Bagley & Sewall Co. He joined the Black-Clawson Co. in 1939 and opened the Portland sales office in 1946. He had recently returned from a trip to New Zealand in the interest of the Company. Mr. Petrie was a member of the Technical Association of the Pulp and Paper Industry.

He is survived by his widow and four sons. Gordon, the eldest, worked with his father for the past few years as a sales engineer on the West Coast.

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# LOCAL SECTION ACTIVITIES

## *Reports of Meetings, Personnel, and Events*

### *Officers of Local Sections*

The local sections of the Technical Association have started their 1951–52 series of meetings. These will run through June, 1952. The annual meetings are held usually in May or June at which time the officers for the next season are elected. The officers who were elected for the 1951–52 terms are as follows:

#### *Pacific*

Chairman—E. O. Ericsson, Puget Sound Pulp & Timber Co., Bellingham, Wash.
Vice-Chairman—Svarre E. Hazelquist, Pulp Div., Weyerhaeuser Timber Co., Longview, Wash.
Secretary-Treasurer—R. M. True, General Dyestuff Corp., Portland, Ore.
Executive Committee—Officers; B. T. Briggs, Rayonier, Inc., Shelton, Wash.; W. F. Holzer, Crown-Zellerbach Corp., Camas, Wash.; J. M. McEwan, Weyerhaeuser Timber Co., Longview, Wash.; H. B. Peterson, Hercules Powder Co., Portland, Ore.; R. I. Thieme, Soundview Pulp Co., Everett, Wash.; and F. J. Weleber, Publishers Paper Co., Oregon City, Ore.
Past-Chairmen—C. R. P. Cash, R. S. Wertheimer, C. W. Morden, R. B. Hansen, Lawrence Killam, M. W. Black, W. R. Barber, Carl Fahlstrom, G. H. McGregor, N. W. Coster, F. A. Olmsted, C. E. Braun, E. P. Wood, C. A. Enghouse, Erik Ekholm, H. W. Bialkowsky, G. H. Gallaway, J. L. McCarthy, H. C. Wall, W. F. Holzer, and R. I. Thieme.
National Executive Committee Representative—W. F. Holzer Crown-Zellerbach Corp., Camas, Wash.

#### *Lake States*

Chairman—Alan P. Adrian, Neenah Paper Co., Neenah, Wis.
Vice-Chairman—Herbert W. Rowe, Nekoosa-Edwards Paper Co. Port Edwards, Wis.
Secretary—Robert J. Seidl, Forest Products Laboratory, Madison, Wis.
Treasurer—L. A. Moss, Whiting-Plover Paper Co., Stevens Point, Wis.
Executive Committee—Officers; Clyde R. Faulkinder, Hoberg Paper Mills, Green Bay, Wis.; J. Richter Salvesen, Marathon Corp., Rothschild, Wis.; and Sidney D. Wells, Institute of Paper Chemistry, Appleton, Wis.
Past-Chairmen—G. K. Hill, Otto Kress, R. J. LeRoux, A. T. Gardner, S. D. Wells, J. R. Fauselow, H. W. Morgan, E. H. Voightman, R. A. Nugent, M. L. Downs, N. L. Malcove, J. H. Graff, T. R. Probst, J. P. Weidner, H. P. Dixson, L. V. Forman, C. J. West, Jr., A. M. Heald, G. R. Sears, and H. C. Crandall.
National Executive Committee Representative—M. L. Downs, Thilmany Pulp & Paper Co., Kaukauna, Wis.

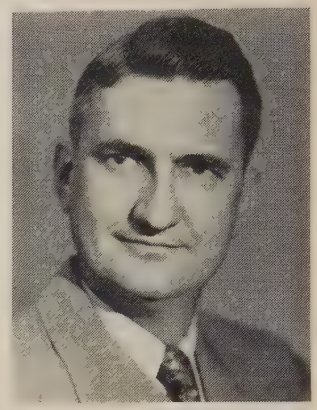
#### *Delaware Valley*

Chairman—A. S. Erspamer, P. H. Glatfelter Co., Spring Grove, Pa.
First Vice-Chairman—H. C. Brill, E. I. du Pont de Nemours & Co., Newport, Del.
Second Vice-Chairman—F. J. Lovegren, W. C. Hamilton & Sons, Miquon, Pa.
Secretary—D. H. Newcomb, Riegel Paper Corp., Milford, N. J.
Treasurer—E. R. Padavic, Container Corp. of America, Manayunk, Pa.
Executive Committee—Officers; John Macadam, National Vulcanized Fibre Co., Yorklyn, Del.; and J. P. Weidner, Container Corp. of America, Manayunk, Pa.
Past-Chairmen—W. R. Maull, G. E. Landt, H. P. Cannon, H. C. Schwabbe, J. d'A. Clark, C. M. Connor, E. J. Albert, J. D. Davis, W. M. Shoemaker, A. L. M. Bixler, John Macadam, and J. P. Weidner.
National Executive Committee Representative—Ward D. Harrison, Riegel Paper Corp., Milford, N. J.

#### *Kalamazoo Valley*

Chairman—John R. Dam, Allied Paper Mills, Kalamazoo, Mich·
Vice-Chairman—A. T. Luey, Sutherland Paper Co., Kalamazoo, Mich.
Secretary—R. H. Hurst, Kalamazoo Vegetable Parchment Co., Kalamazoo, Mich.

*E. O. Ericsson, Puget Sound Pulp & Timber Co.; Chairman, Pacific Section*



*Alan P. Adrian, Neenah Paper Co.; Chairman, Lake States Section*

Treasurer—J. A. Dean, Michigan Paper Co., Plainwell, Mich.
Executive Committee—Officers; F. C. Goodwill, St. Regis Paper Co., Kalamazoo, Mich.; C. E. Mueller, Lockport Felt Co., Kalamazoo, Mich.; W. F. Hathaway, Kalamazoo Vegetable Parchment Co., Kalamazoo, Mich.; J. J. Harrison, Michigan Carton Co., Battle Creek, Mich, and J. A. Wise, Kalamazoo Paper Co., Kalamazoo, Mich.
Past-Chairmen—M. D. Bardeen, E. F. Whittington, H. C. Bradford, C. C. Schneider, H. M. Annis, M. R. Wilkins, W. F. Hathaway, Paul de Guehery, W. A. Kirkpatrick, F. L. Chappel, F. D. Elliott, F. R. Hamilton, E. B. Taylor, R. C. Germanson, H. T. Mashburn, H. L. Mimms, P. W. Bartholomew, S. I. Kukolich, and J. J. Harrison.
National Executive Committee Representative—W. F. Hathaway, Kalamazoo Vegetable Parchment Co., Kalamazoo, Mich.

#### *New England*

Chairman—H. W. Knudson, Hollingsworth & Vose Co., E. Walpole, Mass.
Vice-Chairman—F. S. Klein, Byron Weston Co., Dalton, Mass.
Secretary—A. G. Dreis, Hercules Powder Co., Holyoke, Mass.
Treasurer—H. T. Barker, Bird & Son, E. Walpole, Mass.
Executive Committee—Officers; Gordon L. Benson, St. Regis Paper Co., E. Pepperell, Mass.; C. J. Backus, Whiting & Co., Holyoke, Mass.; C. I. Horton, R. T. Vanderbilt Co., South Norwalk, Conn.; W. C. Hunter, New Haven Pulp & Board Co.,, New Haven, Conn.; Miss Helen V. Kiely, American Writing Paper Co., Holyoke, Mass.; J. T. Loomer, Robert Gair Co., Uncasville, Conn.; S. J. Quattrocchi, Deerfield Glassine Co., Monroe Bridge, Mass.; and George Soyka, Fort Orange Paper Co., Castleton-on-Hudson, N. Y.
Past-Chairmen—F. C. Clark, R. C. Griffin, J. B. Calkin, R. H. Dougherty, N. I. Bearse, W. L. Foote, L. B. Tucker, C. H. Child, P. S. Bolton, and R. J. Proctor.
National Executive Committee Representative—Milton Jacobs, Chas. T. Main, Inc., Boston, Mass.

#### *Ohio*

Chairman—Herbert A. Smith, Mead Corp., Chillicothe, Ohio.
Vice-Chairman—C. E. Brandon, Howard Paper Mills, Dayton, Ohio.
Corresponding Secretary—William C. Martin, Moraine Paper Co., West Carrollton, Ohio.
Recording Secretary—Richard M. Morris, Container Corp. of America, Circleville, Ohio.
Treasurer—R. D. McCarron, Stein, Hall & Co., Cincinnati, Ohio.
Executive Committee—Officers; Philip S. Cade, Harding-Jones Paper Co., Middletown, Ohio; Paul E. Clark, Crystal Tissue Co., Middletown, Ohio; Donald J. Goodman, Sorg Paper Co., Middletown, Ohio; Arthur Thurn, Champion Paper & Fibre Co., Hamilton, Ohio; and D. M. Yost, Sorg Paper Co., Middletown, Ohio.
Past-Chairmen—Vincent F. Waters, H. H. Latimer, K. P. Geohegan, J. E. Burdsall, H. C. Fisher, C. D. Roess, S. I. Olsen, D. M. Yost, P. S. Cade, Arthur Thurn, and Don J. Goodman.

*A. S. Erspamer, P. H. Glatfelter Co.; Chairman, Delaware Valley Section*

*John R. Dam, Allied Paper Mills; Chairman, Kalamazoo Valley Section*

National Executive Committee Representative—K. P. Geohegan, Aetna Div., Howard Paper Mills, Dayton, Ohio.

***Empire State***

Chairman—Joseph S. Reichert, E. I. du Pont de Nemours & Co., Inc., Niagara Falls, N. Y.
Chairman-Elect—Foster P. Doane, Sandy Hill Iron & Brass Works, Hudson Falls, N. Y.
Secretary-Treasurer—Ralph N. Prince, American Cyanamid Co., Castleton-on-Hudson, N. Y.
Executive Committee—Officers; J. F. Butterworth, Socony-Vacuum Oil Co., New York, N. Y.; H. D. Cook, Sweet Bros. Paper Mfg. Co., Phoenix, N. Y.; I. V. Earle, Upson Co., Lockport, N. Y.; M. J. Landberg, General Dyestuff Corp., New York, N. Y.; H. H. Lavery, International Paper Co., Palmer, N. Y.; C. E. Libby, N. Y. State College of Forestry, Syracuse, N. Y.; D. C. Mather, Carthage Paper Makers, Carthage, N. Y.; J. W. Morrow, Newton Falls Paper Co., Newton Falls, N. Y.; R. D. Moynihan, Finch, Pruyn Co., Glens Falls, N. Y.; Harold Spector, St. Regis Paper Co., Watertown, N. Y.; G. K. Storin, Niagara Alkali Corp., Niagara Falls, N. Y.; and W. R. Willets, Titanium Pigment Corp., New York, N. Y.
Past-Chairmen—John H. Schuber, C. E. Libby, J. H. Rich, R. F. Huntley, F. C. Goodwill, H. D. Cook, F. J. Lang, W. O. Hisey, F. J. McCourt, H. A. Spencer, John Campbell, M. L. Jaffe, J. E. Foote, C. E. Foster, and Henry J. Perry.
National Executive Committee Representative—Ralph M. Kumler, American Cyanamid Co., New York, N. Y.

CENTRAL DISTRICT

Chairman—C. E. Libby, N. Y. State College of Forestry, Syracuse, N. Y.
Vice-Chairman—H. D. Cook, Sweet Bros. Paper Mfg. Co., Phoenix, N. Y.
Secretary-Treasurer—Mrs. Barbara H. Wortley, Solvay Process Co., Syracuse, N. Y.

EASTERN DISTRICT

Chairman—H. H. Lavery, International Paper Co., Palmer, N. Y.
Vice-Chairman—R. E. March, Marinette Paper Co., Fort Edward, N. Y.
Secretary-Treasurer—K. L. Seeber, Sandy Hill Iron & Brass Works, Hudson Falls, N. Y.
Executive Committee—Officers and Robert Moynihan, Finch, Pruyn & Co., Glens Falls, N. Y.

METROPOLITAN DISTRICT

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Vice-Chairman—R. W. Kumler, American Cyanamid Co., New York, N. Y.
Secretary-Treasurer—J. F. Butterworth, Socony-Vacuum Oil Co., New York, N. Y.
Executive Committee—Officers; John J. Doherty, Union Bag & Paper Co., New York, N. Y.; R. T. Emerson, Manifold Supplies Co., Brooklyn, N. Y.; P. L. Haggerty, George La Monte Sons, Nutley, N. J.; and L. S. Reid, Metropolitan Life Insurance Co., New York, N. Y.

NORTHERN DISTRICT

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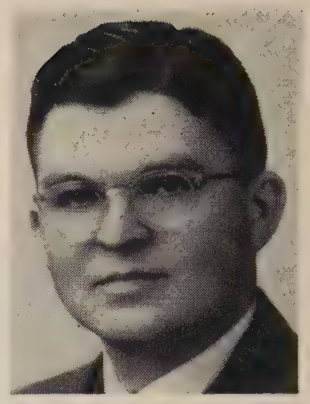
National Executive Committee Representative—Milton Jacobs, Chas. T. Main, Inc., Boston, Mass.

***Chicago***

Chairman—V. V. Vallandigham, Kelco Co., Chicago, Ill.
Vice-Chairman—A. A. Deutsch, Container Corp. of America, Chicago, Ill.
Secretary—C. H. Krebs, Atlas Boxmakers, Chicago, Ill.
Treasurer—J. R. Fulghum, Socony-Vacuum Oil Co., Chicago, Ill.
Past-Chairmen—H. R. Alley, H. E. Weston, F. D. Long, J. L. Kubicka, Warren R. Price, G. A. Zinkel, and Albert K. Roach.
Executive Committee—Officers; A. K. Roach, Wm. H. Welsh Co., Chicago, Ill.; Peter Trucano, Morris Paper Mills, Morris, Ill.; R. D. Carter, Keyes Fibre Co., Hammond, Ind.; A. L. Magnuson, Kelco Co., Chicago, Ill.; Warren Price, Applied Research Service, Chicago, Ill.; and M. W. Snover, Williamson Adhesives Co., Chicago, Ill.
National Executive Committee Representative—Werner Kaufmann, Kupfer Bros. Paper Co., Chicago, Ill.

*H. W. Knudson, Hollingsworth & Vose Co.; Chairman, New England Section*



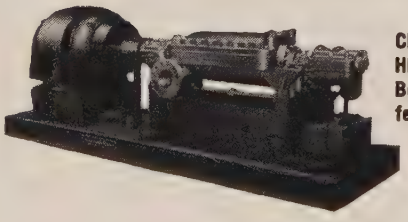
*Herbert A. Smith, Mead Corp.; Chairman, Ohio Section*

***Lake Erie***

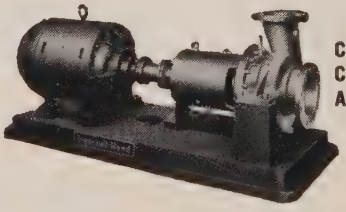
Chairman—William Hasselo, Container Corp. of America, Cleveland, Ohio.
First Vice-Chairman—Joseph F. Thompson, Minerva Wax Paper Co., Minerva, Ohio.
Second Vice-Chairman—Russell L. Lewis, Ohio Boxboard Co., Rittman, Ohio.
Secretary—Lynn E. Rollig, Ohio Boxboard Co., Rittman, Ohio.
Treasurer—William Schoenberg, Lord & Schoenberg, Cleveland, Ohio.


RIGHT THROUGH THE MILL

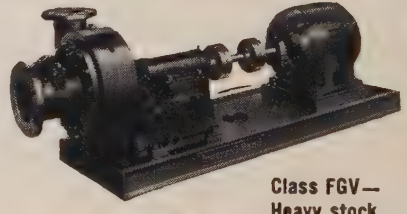
FROM BOILER FEED TO PAPER MACHINE . . .



Class HMTA—Boiler feed



Class CSFL—Acid



Class FGV—Heavy stock

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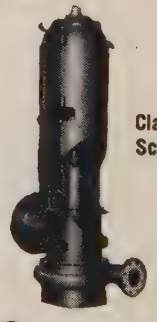
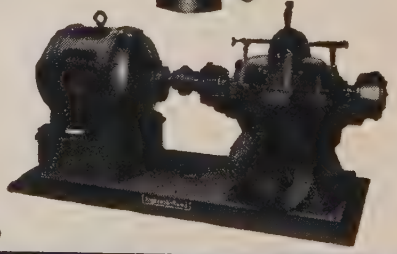
An Ingersoll-Rand engineer will be glad to consult with you about your problems and the solution that I-R pumps can provide.



Class VGV—Screened stock

Class ALV—White water and general service



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*C. E. Libby, New York State College of Forestry; Chairman, Central District, Empire State Section*

Executive Committee—L. K. Burnett, Ohio Boxboard Co., Rittman, Ohio; Arthur Cheely, Hankins Container Co., Cleveland, Ohio; David N. Cooper, Buckeye Ribbon and Carbon Co., Cleveland, Ohio; Leonard R. Gwaltney, Ohio Boxboard Co., Rittman, Ohio; Richard Jones, Sinclair & Valentine Co., Rittman, Ohio; W. O. Manor, Consolidated Paper Co., Monroe, Mich.; J. Noll, Monroe Falls Paper Co., Monroe Falls, Ohio; Dennis Reidy, Gair Cleveland Containers, Inc., Cleveland, Ohio; David Shotwell, International Printing Ink Co., Cleveland, Ohio; C. Peter Spring, Chase Bag Co., Chagrin Falls, Ohio; and George Traub, Traub Box Co., Cleveland, Ohio.

Past-Chairman—Lewis K. Burnett.

National Executive Committee Representative—Richard P. Price, Hammermill Paper Co., Erie, Pa.

***Papermakers and Associates of Southern California***

Chairman—Wm. C. Birdsey, Pioneer-Flintkote Co.. Los Angeles, Calif.

Vice-Chairman—J. T. Gooey, Angelus Paper Box Co., Los Angeles, Calif.

Secretary-Treasurer—Wayne Kuefner, Pioneer-Flintkote Co., Los Angeles, Calif.

Executive Committee—Lloyd J. Deen, Volney Felt Mills, Compton, Calif.; Edwin C. Lovret, U. S. Gypsum Co., South Gate, Calif.; and Claude Sharp, Angelus Paper Box Co., Los Angeles, Calif.

Past-Chairmen—Herman L. Joachim, V. C. Farmer, C. G. Frampton, W. A. Kinney, F. H. Wheelock, R. S. Buckley, John Van Amsem, W. G. Hartford, Bruce F. Brown, Jr., Robert W. Stevens, and Claude Sharp.

## *Review of Local Section Meetings in 1950–51*

The following is a record of the meetings held by the TAPPI Local Sections during the past year. Local Section meetings begin usually in September and end in June. With the exception of outings the Sections recess during July and August. The report of the 1949–50 meetings appeared in the September, 1950, issue of *Tappi*.

### *Pacific*

The Pacific Section was organized at Seattle, Wash., in June, 1929. The annual meeting is usually held in May.

*Sept. 11–12 and 14–15, 1950:* (At Portland, Ore., and Seattle, Wash., respectively.) Fourth Annual Seminar on "Application of Physics to the Processes of Pulp and Paper," by J. A. Van den Akker, Institute of Paper Chemistry, Appleton, Wis.

*Sept. 13, 1950:* (Bagley Hall, University of Washington, Seattle, Wash.) Symposium on "Pulp Purification," R. S. Hatch, Consulting Engineer, Monterey, Calif., Moderator. (1) "Experiments on the Purification of Sulphate Pulps for Viscose Rayon," by F. A. Simmonds, Forest Products Laboratory, Madison, Wis.; (2) "Determination of Alpha Cellulose," by John J. McNair, Pulp Div., Weyerhaeuser Timber Co., Longview, Wash.; (3) "Chlorine Dioxide and Its Uses in the Bleaching of Wood Pulp," by A. H. Lundberg, Chemical Engineer, Seattle, Wash. Dinner meeting at Edmond Meany Hotel. "Color," by J. A. Van den Akker, Institute of Paper Chemistry, Appleton, Wis.


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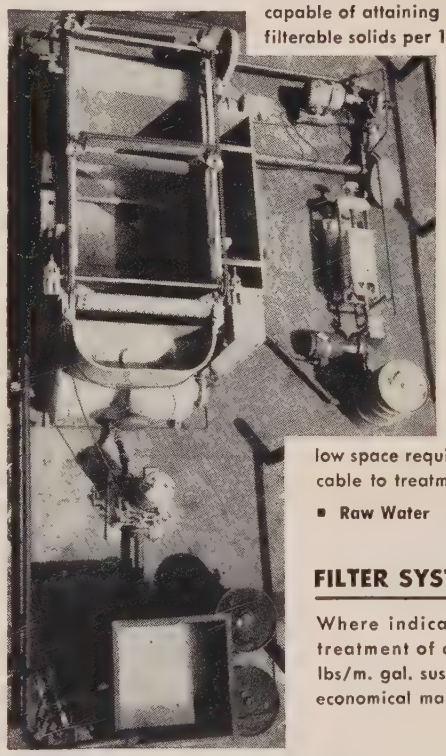

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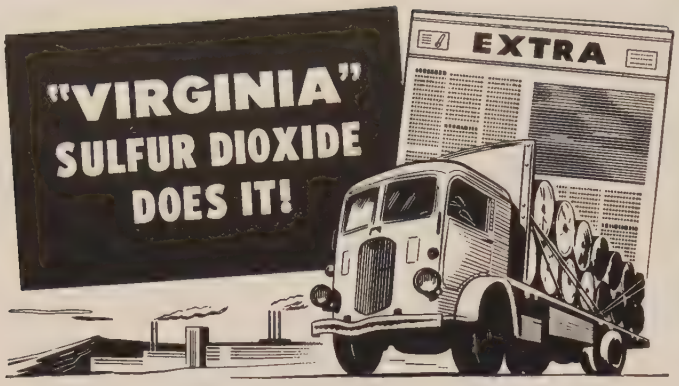


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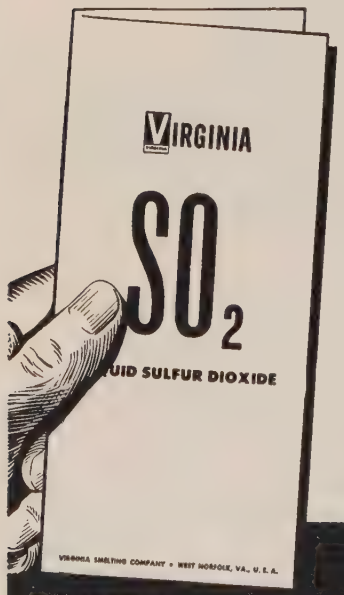


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*W. R. Willets, Titanium Pigment Corp.; Chairman, Metropolitan District, Empire State Section*

*J. Wayne Morrow, Newton Falls Paper Co.; Chairman, Northern District, Empire State Section*

*Nov. 7, 1950:* (Camas, Wash.) Panel Discussion on "Printing and Print Papers," E. H. Nunn, Crown Zellerbach Corp., West Linn, Ore., Moderator. (1) "Ink Problems in Printing," by Maurice Adler, California Ink Co., Berkeley, Calif.; (2) "Problems Arising in the Printing of Paper," by Milton Bell, Abbott, Kerns and Bell, Portland, Ore.; (3) "Quality Control of Printing Papers," by G. R. Cranor, Oregon Pulp and Paper Co., Salem, Ore.; (4) "Pulp Qualities Affecting the Characteristics of Printing Papers," by B. H. Wright, Crown Zellerbach Corp., West Linn, Ore.; Dinner Speaker—"Forty Copies a Second, Every Week," by F. E. Church, Asst. Production Manager, Time, Inc., New York, N. Y.

*Feb. 6, 1951:* (Hotel Winthrop, Tacoma, Wash.) Annual Engineering Meeting. "Some Aspects of Burning Wood Waste by the Spreader Stoker," by Conant Dodge, H. A. Smyth, and L. R. Guthrie, Weyerhaeuser Timber Co., Tacoma, Wash.; "Practical Problems of Motor Applications in Paper Mills," by John Schuh, Longview Fibre Co., Longview, Wash.; "Experience with a Stainless Steel Lined Digester in Sulphite Service," by Bryan L. Rauschert, Rayonier, Inc., Port Angeles, Wash.; and "A Modern Spreader Installation Utilizing Wood Waste Fuel," by C. L. Judson and R. B. Boals, Eugene Water Board, Eugene, Ore.; Dinner Speaker—"The Power Situation in the Pacific Northwest," by O. B. Falls, General Electric Co., Seattle, Wash.

*April 13, 1951:* (Lower Columbia Junior College, Longview, Wash.) Annual Shibley Award Program. Walter F. Holzer, Crown Zellerbach Corp., Camas, Wash., Moderator: "Seam Adhesives for Multiwall Bags," by K. M. Shold, Crown Zellerbach Corp., Port Townsend, Wash.; "Special Problems in the Operation of an MgO-Base Sulphite Acid Plant," by John L. McClintock, Jr., Pulp Dif., Weyerhaeuser Timber Co., Longview, Wash.; "Photographic Standards for Dirt Control," by W. F. Cyrus, Crown Zellerbach Corp., West Linn, Ore.; "Sources of Wood Dirt in Unbleached Pulp," by Carter A. Watson, Puget Sound Pulp & Timber Co., Bellingham, Wash. Dinner Speaker—R. C. McCall, Chairman, Department of Speech, University of Oregon, Eugene, Ore.

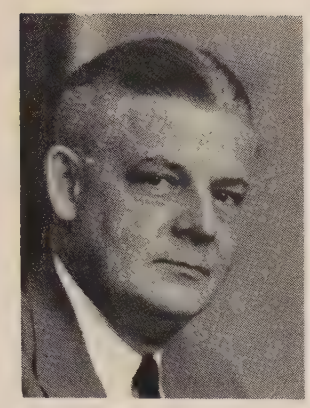
## *Lake States*

The Lake States Section was organized in Menasha, Wis., on Oct. 17, 1930. Meetings are usually held on the second Tuesday of each month at the American Legion Club House in Appleton, Wis., unless otherwise indicated. No meetings are held in December and February. The November and April meetings began at 1:30 p.m., the other meeting began at 6:30 p.m.

*Oct. 10, 1950:* Panel Discussion on "Recent Developments in Pulp Bleaching," H. C. Crandall, Mosinee Paper Mills, Mosinee, Wis., Moderator. (1) "Kraft Bleaching," by T. A. Pascoe, Nekoosa-Edwards Paper Co., Port Edwards, Wis.; (2) "Groundwood and Semichemical Pulp Bleaching," by R. M. Kingsbury, Forest Products Laboratory, Madison, Wis.; (3) "Sulphite Bleaching," by Mace Harris, Northwest Paper Co., Cloquet, Minn.

*Nov. 14, 1950:* (Northland Hotel, Green Bay, Wis.) Visit to Green Bay Pulp and Paper Co. mill. Symposium on "Semichemical Pulp and Paper." Papers: "Semichemical Pulp in the Manufacture of Specialty Papers," by Karl Fries, Rhinelander Paper Co., Rhinelander, Wis.; "Semichemical Pulping Opera-

*I. V. Earle, Upson Co.; Chairman, Western District, Empire State Section*



*George A. Day, Brown Co.; Chairman, Maine-New Hampshire Section*

tions and Equipment," by W. W. Marteny, National Container Corp., Tomahawk, Wis.; "Bleaching of Neutral Sulphite Semichemical Pulp," by S. R. Parsons, Consolidated Water Power and Paper Co., Wisconsin Rapids, Wis. Dinner Speaker—"A Banker Looks at the Paper Industry Finances," by A. Newell Rumpf, Vice-President, Harris Trust and Savings Bank, Chicago, Ill.

*Jan. 9, 1951:* "Power and Steam Generation," by Dan S. Helmick, Helmick, Edeskuty and Lutz, Minneapolis, Minn.

*March 13, 1951:* Institute of Paper Chemistry Program: H. C. Crandall, Chairman. "Microbiological Control in the Pulp and Paper Industry," by B. F. Shema; "The Story of Ethyl Vanillate," by Irwin A. Pearl; "Pollution Suits," by Willis M. Van Horn.

*April 10, 1951:* (Wausau Club, Wausau, Wis.) Visit to Marathon Corp. Carton plant. Symposium on "Printing." "Printing Paper End Use Requirements," by Freeling M. Truesdale, Nekoosa-Edwards Paper Co., Port Edwards, Wis.; "Paper for Offset Lithography," by Robert F. Reed, Lithographic Technical Foundation, Chicago, Ill. Dinner Meeting (20th Anniversary)—" Early Days of Lake States TAPPI," by Rev. G. K. Hill, First Chairman of Lake States TAPPI; "The Years Ahead," by Allen Abrams, Marathon Corp., Rothschild, Wis.

*May 15, 1951:* "Applications of Engineering Thinking," by A. E. Bachmann, Missisquoi Corp., Sheldon Springs, Vt. Election of Officers.

## *Delaware Valley*

The Delaware Valley Section was organized at Philadelphia in June, 1931. Meetings are held monthly at the Engineers Club, Philadelphia, Pa., on the fourth Thursday of each month.

*Sept. 28, 1950:* Visit to Triangle Publishers, Inc., Gravure Div., Philadelphia. Dinner Meeting at the Engineers Club—"Human Relations in Industry," by Harrison F. Dunning, Manager of Paper Mills, Scott Paper Co., Chester, Pa.

*Oct. 26, 1950:* "Pulp Refining and the Curlator," by James D. Coghill, Curlator Corp., Rochester, N. Y.

*Nov. 30, 1950:* Panel Discussion on "Routine Control Testing Methods," C. M. Connor, W. C. Hamilton & Son, Miquon, Pa., Moderator. Panel Members—N. V. Edmonson, Scott Paper Co., Chester, Pa.; R. E. Green, Thwing-Albert Instrument Co., Philadelphia, Pa.; E. R. Padavic, Container Corp. of America, Manayunk, Pa.; J. T. Ward, Riegel Paper Corp., Milford, N. J.; K. S. Whisler, P. H. Glatfelter Co., Spring Grove, Pa.

*Jan. 25, 1951:* "The Paper Industry's Present Status in the Rearmament Program," by Louis T. Stevenson, American Paper & Pulp Association.

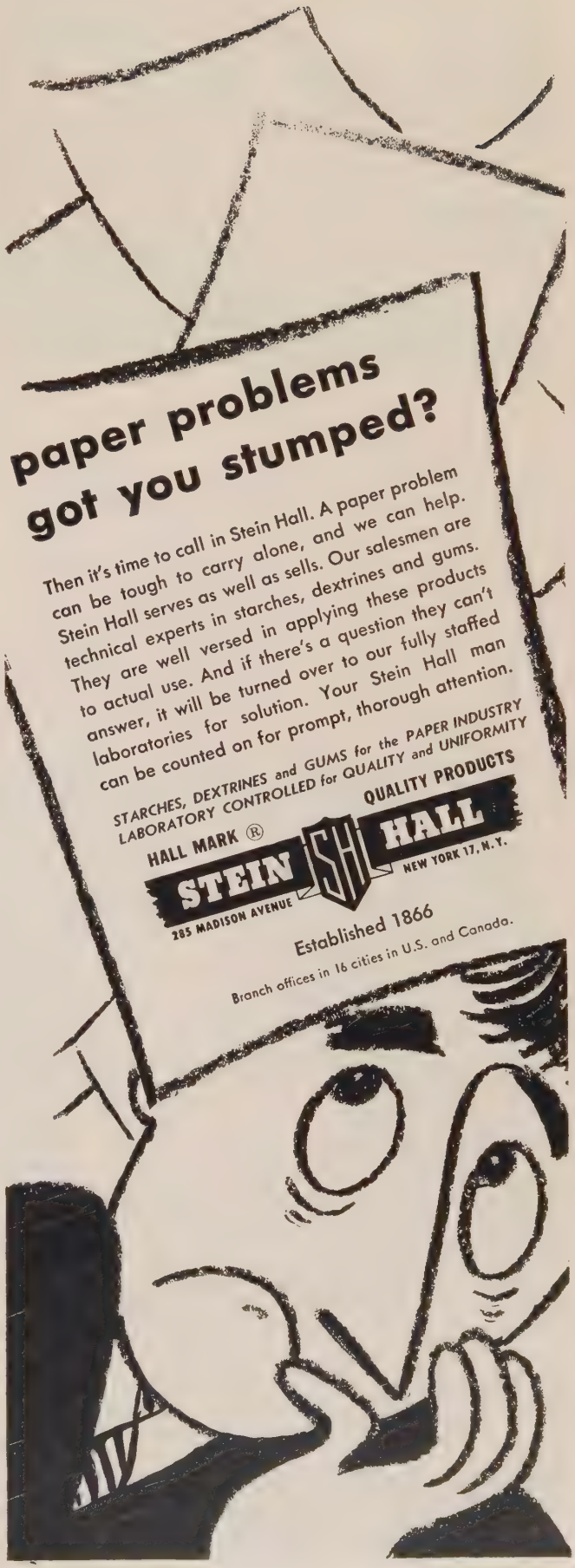
*March 22, 1951:* "Production and Procurement of Paper Items," by E. T. A. Coughlin, Chief of Paper and Paper Products Unit, Office of the Quartermaster General, Washington, D. C.

*April 26, 1951:* "Paper Machine Felts—Their Influence on Paper Making Problems," by Lawrence M. Woodside, Albany Felt Co., Albany, N. Y.

*May 24, 1951:* "Pulp for Fine Papers and Dissolving Purposes, Finely Divided Cellulose," by M. A. Hescock, Brown Co., Berlin, N. H. Motion picture—"Timber as a Crop."

## *Kalamazoo Valley*

The Kalamazoo Valley Section was organized at Kalamazoo, Mich., on May 4, 1931. Its meetings are held on the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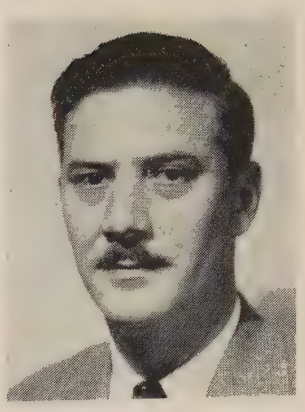

*V. V. Vallandigham, Kelco Co.; Chairman, Chicago Section*

*William Hasselo, Container Corp. of America; Chairman, Lake Erie Section*

first Thursday of each month at either the Columbia or Harris Hotels, Kalamazoo.

*Oct. 5, 1950:* "Paper Printing Problems from the Standpoint of the Merchant and Printer," by W. H. Bureau, Butler Paper Co., Chicago, Ill.

*Nov. 2, 1950:* "Semichemical Pulping for Book Paper Mills," by L. N. Murtfeldt, Consolidated Water Power & Paper Co., Wisconsin Rapids, Wis.; "Semichemical Pulping for Board Mills," by S. G. Steffes, Otsego Falls Paper Co., Otsego, Mich.

*Dec. 7, 1950:* "Panelyte—Its Technology and Use," by M. R. Yorke, Panelyte Div., St. Regis Paper Co., Kalamazoo, Mich.

*Jan. 18, 1941:* "Let's Build a Better America," by Allen A. Stockdale, National Association of Manufacturers. Joint meeting with Michigan Div., Am. Pulp and Paper Mill Superintendents Association. Dwight Stocker, President, Michigan Paper Co., Plainwell, Mich., Toastmaster.

*Feb. 1, 1951:* Symposium on "Pulp and Paper Mill Waste Waters." "Waste Water Surveys," by E. N. Ross, Lee Paper Co., Vicksburg, Mich.; "Semichemical Pulp Liquor Wastes," by D. L. Voigts, American Boxboard Co., Filer City, Mich.; "Sveen Pederson Savealls," by Gordon Hay, Michigan Carton Co., Battle Creek, Mich.; and "The Effect of Waste Recovery and Treatment Processes on Stream Improvement," by A. J. Palladino, National Council for Stream Improvement, New York, N. Y.

*March 1, 1951:* "Tub, Calender, and Beater Starches with Particular Reference to Penford Gums," by C. R. Vander Meulen, Penick & Ford Ltd., Inc., Cedar Rapids, Iowa.

*April 5, 1951:* "The Influence of Adhesives in Coated Papers on Printing Performance," by Glenn Davidson, Aurora, Ill.; Panel Discussion on "Coating." Members of the Panel—A. T. Luey, Sutherland Paper Co.; L. H. Mimms, Kalamazoo Paper Co.; Harrison Kindig, Mac Sim Bar Paper Co.; Henry Neudorf, Rex Paper Co.; Martin Galbraith, Sutherland Paper Co.; R. J. Grimm, St. Regis Paper Co. Joint meeting with Michigan Div., Am. Pulp Paper and Mill Superintendents Association.

*May 3, 1951:* Kalamazoo Valley Section Award to Wilber Kite for highest scholastic record in Pulp and Paper Course, Western Michigan College. Presentation by Stephen I. Kukolich, Lee Paper Co., Vicksburg, Mich. Discussion of theses by students: "Dewaxing Waste Papers," by Donald Huyser; "Brightness Testers," by Wyman Uhl; "Elastometers and Beater Retention," by Raymond Wagner; "The G.E. Puncture Tester," by Roger McVicker; "Water Resistant Stock Coatings," by Elton Krogel; "Variations in Yield in Deinking," by William Noel; "Enzyme Converted Starches," by Edward Stephenson; and "Deinked Stock Opacity vs. Bleaching," by Wilber Kite.

*June 7, 1951:* Annual outing and "Fun Day," Gull Lake Country Club, Kalamazoo, Mich. Election of Officers.

## *New England*

The New England Section was organized at Holyoke, Mass., on Dec. 9, 1932. The following meetings were held during the current year.

*Sept. 29, 1950:* (Red Lion Inn, Stockbridge, Mass.) (1) "Further Investigations in the Microscopy of Beaten Fibers," by F. L. Simons, Crane & Co., Dalton, Mass.; (2) "The Cowles Knifemill," by Edwin C. Cowles, The Cowles Co., Cayuga, N. Y.

*Nov. 17, 1950:* (Roger Smith Hotel, Holyoke, Mass.) "Operating Principles as Related to Quality Control," by A. E. Bachmann, Missisquoi Corp., Sheldon Springs, Vt.

*Jan. 19, 1951:* (Roger Smith Hotel, Holyoke, Mass.) "The

Value of Instruments for Testing in the Control of the Paper Making Process," by Norman I. Bearse, Champion International Co., Lawrence, Mass.; "Quality Control and Its Application to Paper Manufacture," by M. E. Blew, Strathmore Paper Co., W. Springfield, Mass.

*April 18–20, 1951:* (Statler Hotel, Boston, Mass.) National Coating Conference sponsored by the New England Section. John P. Heuer, APW Products, Inc., Albany, N. Y., General Chairman; A. D. Bonanno, Champion-International Co., Lawrence, Mass., R. T. Trelfa, Hercules Powder Co., Wilmington, Del., Chairman of Symposium on "Raw Stock Requirements for Coated Paper," Program Chairman. "Raw Stock Requirements," Introduction to Symposium, by Norman I. Bearse, Champion-International Co., Lawrence, Mass.; "Requirements for Hanging Stock," by Thomas La Haise, Imperial Paper & Color Corp., Plattsburg, N. Y.; "Requirements for Off-Machine Book," by A. Lewenstein, Appleton Coated Paper Co., Appleton, Wis., and P. Hansen, Bergstrom Paper Co., Neenah, Wis.; "Requirements of Off-Machine Board," by A. T. Luey, Sutherland Paper Co., Kalamazoo, Mich.; "Requirements for On-Machine Board," by W. C. Hunter, New Haven Pulp & Board Co., New Haven, Conn.; "Requirements for On-Machine Book," by J. E. Wilber, St. Regis Paper Co., Deferiet, N. Y.; "Requirements for On-Machine, Publications," by Paul J. Thoma, Time, Inc., Springdale Conn.; "The Trist Paper Coating System," by A. Ronald Trist, Trist Colloid Product Patents, New York, N. Y.; "Brightness and Opacity of Certain Pigmented Coatings," by J. Frankewicz and J. Senuta, Champion-International Co., Lawrence, Mass.; "Partial Structure and Flow Properties of Coating Clays," by C. G. Albert, Edgar Bros. Co., McIntyre, Ga.; "A Preliminary Study of the Particle Size of Clay, Its Determination and Effects," by F. Masterman, Provincial Paper Ltd., Toronto, Ont.; "The Mechanism of Gloss Development in Clay-Coated Paper," by S. C. Lyons, Georgia Kaolin Co., Dry Branch, Ga.; "The Requirements of Coated Paper for Offset Lithography," by W. H. Bureau Paper Co., Chicago, Ill.; "Comparative Study of Various Starches," by Gordon I. Hoover, Provincial Paper Ltd., Georgetown, Ont.; "The Hercules Print Tester," by E. J. Barber and J. W. Davis, Hercules Powder Co., Wilmington, Del. Luncheon Address—"Feast or Famine," by George Olmsted, Jr., S. D. Warren Co., Boston, Mass.

*June 8–9, 1951:* (Griswold Hotel and Country Club, Groton, Conn.) Symposium on "Statistical Quality Control as Applied to Paper Manufacturing and Converting." Panel Members—Geoffrey Beall, University of Connecticut, Storrs, Conn.; W. H. Coughlin, Thompson Products Co., Cleveland, Ohio; F. S. Klein, Byron Weston Co., Dalton, Mass.; M. E. Blew, Strathmore Paper Co., W. Springfield, Mass.; O. H. Somers, Western Printing & Lithographing Co., Poughkeepsie, N. Y.; W. R. Purcell, Brown Co., Berlin, N. H.; M. S. Renner, Dewey & Almy Chemical Co., Cambridge, Mass.; Harold Cobb, S. D. Warren Co., Cumberland Mills, Me. Papers: "Correlation in Paper Statistics," by W. H. Coughlin, Thompson Products Co., Cleveland, Ohio; "Differences in Controlling Paper Quality and Quality of Other Products, by Geoffrey Beall, University of Connecticut, Storrs, Conn.

## *Ohio*

The Ohio Section was organized on Nov. 30, 1934, at Middletown, Ohio. Meetings were held during the past year at the Manchester Hotel in Middletown.

*Oct. 10, 1950:* The General Electric Co. and the Cincinnati Gas and Electric Co. collaborated in a demonstration program on "Industrial Lighting for Paper Mills." E. A. Lindsay, Industrial Lighting Specialist of the G.E. Nela Park, Cleveland, Ohio, Laboratory, acted as narrator. Joint meeting with the Miami Valley Div., Am. Pulp and Paper Mill Superintendent Association.

*Nov. 9, 1950:* Fifteenth Anniversary Meeting. Introductory Remarks, by Donald Goodman, Chairman, Sorg Paper Co., Middletown, Ohio; Introduction of 1950 Officers and Past-Chairman by Vincent F. Waters, First Chairman, *Southern Pulp and Paper Manufacturer*, Atlanta, Ga.; "The Stewardship of a Local Section," by R. G. Macdonald, Secretary-Treasurer, Technical Association of the Pulp and Paper Industry, New York, N. Y., and "Observations on the European Paper Industry." by Herbert T. Randall, Vice-President, Champion Paper & Fibre Co., Hamilton, Ohio.

*Dec. 12, 1950:* "Fiber to Fiber Bonding," by Herman Mark, Director of the Institute of Polymer Research, Polytechnic Institute of Brooklyn, Brooklyn, N. Y.

*Jan. 9, 1951:* "Beater Addition Plastics and Specialty Papers." Talks by Francis H. Snyder, Snyder Chemical Co., Bethel, Conn., and William H. Aiken, Goodyear Tire & Rubber Co., Akron, Ohio.

*Feb. 8, 1951:* Joint meeting with the Cincinnati Club of Printing House Craftsmen, Cincinnati, Ohio. "Methods in Statistical Control," by Ralph J. Knoll, Scott Paper Co., Chester, Pa.; "The


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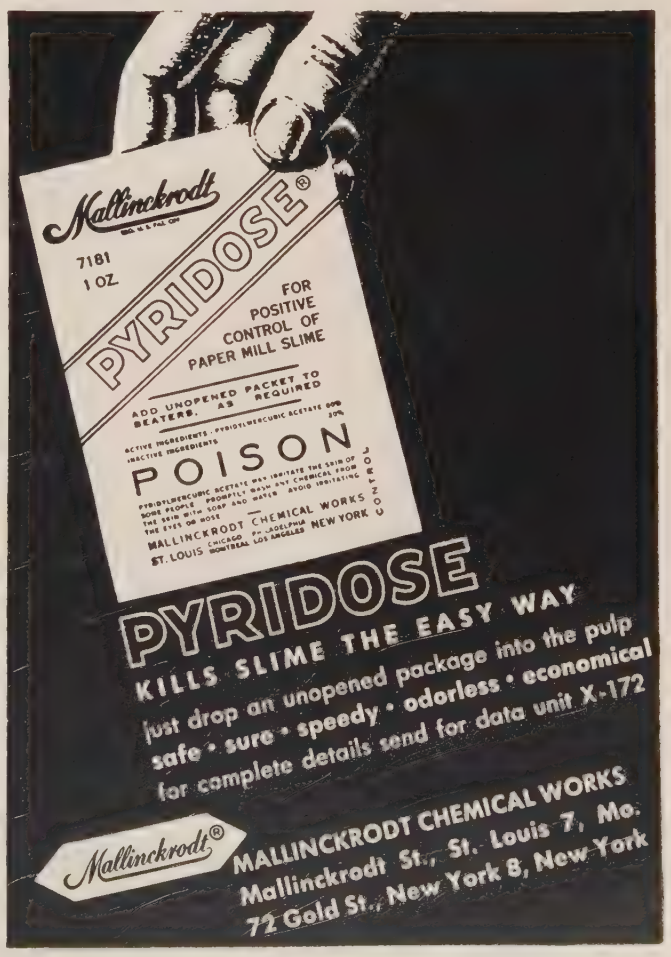
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Use of the G.E. Spectrophotometer," by John M. Papp, General Electric Co., Schenectady, N. Y.

*March 8, 1951:* "Military Planning in the Paper Industry," by E. T. A. Coughlin, Chief of the Paper and Paper Products Unit, Chemical and Plastics Section, Research and Development Branch, Military Planning Div., Office of the Army Quartermaster General.

*April 10, 1951:* Motion picture and lecture on the use of color by O. C. Holland, International Printing Ink Co., New York, N. Y.

*May 10, 1951:* Annual meeting and entertainment. Election of Officers. Presentation of a Longine watch to Kenneth P. Geohegan, Howard Paper Mills, Dayton, Ohio, president of TAPPI.

## *Empire State*

The Empire State Section began holding meetings in 1935 and received its charter on April 2, 1938. In 1943 the Section was reorganized on a regional basis with meetings being held in four districts of New York State. In 1948 the Metropolitan District was added.

*May 18, 1951:* (Drumlins Country Club, Syracuse, N. Y.) New York State College of Forestry Seniors' Dinner Meeting with students and staff as guests of the Empire State Section, Henry J. Perry, *Paper Trade Journal*, New York, N. Y., Chairman. Brief talks about the industry and the Technical Association. The Central District was reactivated at this meeting.

*June 28-30, 1951:* (Whiteface Inn, Lake Placid, N. Y.) "Industry's Role as Related to New York State's Pulpwood Supply," by G. A. Pesez, International Paper Co., Glens Falls, N. Y.; "Public and Private Forestery Get Together," by J. Victor Skiff, State of New York Conservation Department, Albany, N. Y.; "Utilization of Hardwoods for Chemical Pulp," by F. W. O'Neil, New York State College of Forestry, Syracuse, N. Y.; "Trends in the Paperboard Industry," by P. S. Bolton, Robert Gair Co., Uncasville, Conn.; "Burning of Sulphite Waste Liquor," by W. J. Darnstadt and F. H. Richter, Babcock & Wilcox Co., New York, N. Y.; "Impact of Defense Requirements on the Pulp and Paper Industry," by Clinton K. Royce, Head, Packaging Section, Office of Navy Material, Navy Department, Washington, D. C.; "A Few Thoughts on Stream Pollution," by Horace A. Spencer, Knowlton Bros. Co., Watertown, N. Y.; "Printing Ink and Equipment Developments and Their Effect on Paper Requirements," by Lou Engelhart, International Printing Ink Co., Elizabeth, N. J.; "Reciprocal Paper-Plastics Developments," by E. C. Jahn, New York State College of Forestry, Syracuse, N. Y.

EASTERN DISTRICT (Milfrank's Restaurant, S. Glens Falls, N. Y., Third Thursday of Month)

*Oct. 19, 1950:* "Trends in European Paper Mill Operations," by Vance P. Edwardes, Consulting Engineer, Corinth, N. Y.; Foster P. Doane, Sandy Hill Iron & Brass Works, Hudson Falls, N. Y.

*Nov. 16, 1950:* "What We Do Not Know About Paper Manufacturing," by Harry Spencer, Howard Smith Paper Mills, Cornwall, Ont.

*Dec. 14, 1950:* "Some Fundamentals of Coating Machines and Their Uses," by Charles A. Dickhaut, John Waldron Corp., New Brunswick, N. J.

*Jan. 18, 1951:* Ladies Night. Presentation by the Westinghouse Electric Corp., East Pittsburgh, Pa. "Adventures in Research," conducted by Robert Dostal.

*Feb. 15, 1951:* "Paper and Board Characteristics That Affect Inks and Printability," by L. F. Englehart, International Printing Ink Co., Elizabeth, N. J.

*March 15, 1951:* Panel Discussion on "Groundwood Specialties." Allen Lowe, Sandy Hill Iron & Brass Works, presided as moderator. "Groundwood Process Control," by Clyde Davis, Finch, Pruyn & Co., Glens Falls, N. Y.; "Preparation of Groundwood for Groundwood Specialties," by Oscar Anderson, Jr., International Paper Co.; "Bleached Groundwood," by Herbert F. Jacques, Pulp and Paper Div., Diamond Match Co., Plattsburg, N. Y.

*April 19, 1951:* "Pumps and Pump Troubles," by S. H. Grimnes, Diamond Match Co., Plattsburg, N. Y.

*May 17, 1951:* Visit to the International Paper Co. Mill, Palmer, N. Y., and showing of the Company film "In Partnership with Nature." At the dinner meeting a panel group consisting of Henry Perry, *Paper Trade Journal*, New York, N. Y., and Homer Rice, E. I. du Pont de Nemours & Co., Inc., Watertown, N. Y., discussed "Political and Economic Problems of the Paper Industry."

METROPOLITAN DISTRICT (Fraunces Tavern, New York, N. Y., Second Tuesday of Month)

*Sept. 12, 1950:* Panel Meeting on "New Papers from the Use

of Chemicals," by R. W. Kumler, American Cyanamid Co., New York, N. Y., Moderator. Panel Members—C. G. Landes, American Cyanamid Co., Stamford, Conn.; T. S. Morse, Hercules Powder Co., Wilmington, Del.; E. K. Stilbert, Dow Chemical Co., Midland, Mich.; R. H. Walsh, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del. Subjects covered: (1) Beater Addition of Resins and Dispersions; (2) Bonding and Wet Strength Resins; (3) Latices for Impregnating and Coating of Paper; (4) Cellulose Derivatives; (5) Paper Softeners; and (6) Fluidifiers for Starch and Casein Solutions.

*Oct. 9, 1950:* Panel Discussion on "Economic and Political Problems of the Pulp and Paper Industry," Henry Perry, *Paper Trade Journal*, New York, N. Y., Moderator. Members of the Panel—Julius Kahn, Attorney, New York, N. Y.; George Brooks, Educational Director, International Brotherhood of Pulp, Sulphite, and Paper Mill Workers, Fort Edward, N. Y.; E. W. Tinker, Executive Secretary, American Paper and Pulp Association, New York, N. Y.

*Nov. 14, 1950:* "Technical Problems of the Newsprint Industry," by Gerard Larocque, News Syndicate, New York, N. Y.

*Jan. 9, 1951:* Symposium, "New Ideas in the Use of Paper for Automatic Packaging," Robert de S. Couch, Moderator. Speakers: R. A. Morck, R. B. Davis Co., New York, N. Y.; Miles H. Walker, Arnold Bakeries, Inc., New York, N. Y.; Walter Byrd, Johnson & Johnson, New Brunswick, N. J.

*March 6, 1951:* "Armed Services Procurement Problems," by Col. T. P. Coates and Lt. Col. Robert B. Hamilton, New York Quartermaster Procurement Agency, New York, N. Y.

*April 3, 1951:* Panel Discussion on "Waste Paper." Panel Members—S. I. Hershman, I. Hershman & Co., New Haven, Conn.; J. A. Cauwels, Purchasing Agent, Federal Paper Board Co., Bogota, N. J.; Anthony Gaccione, President, Toga Paper Stock Co., Inc., New York, N. Y.

*May 1, 1951:* "Questioned Documents," by Albert D. Osborn, Examiner of Questioned Document Consultant, New York, N. Y.

NORTHERN DISTRICT (Hotel Woodruff, Watertown, N. Y., Second Thursday of Month)

*Oct. 12, 1950:* "Research and Facilities at the School of Forestry," by F. W. O'Neil, New York State College of Forestry, Syracuse, N. Y.

*Nov. 9, 1950:* "Points of Interest in My Trip to Brazil and South Africa," by H. D. Cook, Sweet Brothers Paper Co., Inc., Phoenix, N. Y.

*Dec. 14, 1950:* "Practical Aspects of the Application of Wax Sizes in Paper Manufacture," by George E. Fromm and Harold Sinclair, American Cyanamid Co., New York, N. Y.

*Jan. 11, 1950:* "The Cowles Knife Mill," by A. W. Infanger, Cowels Co., Cayuga, N. Y.

*Feb. 8, 1951:* Salesmen's Smoker.

*March 8, 1951:* "How the Engineer Can Help the Doctor Save Your Life," by Jack T. Wilson, Allis-Chalmers Mfg. Co., Milwaukee, Wis. Election of Officers.

*April 12, 1951:* "The Political and Economic Problems of the Paper Industry," by Henry J. Perry, *Paper Trade Journal*, New York, N. Y., and H. M. Rice, E. I. du Pont de Nemours & Co., Watertown, N. Y.

*May 10, 1951:* "Progress in Better Living," by Louis P. Shannon, Public Relations Manager, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.; showing of motion pictures of the Thousand Island Meeting of the Empire State Section by Walter B. Morehouse, Nopco Chemical Co., Harrison, N. J. Ladies Night.

WESTERN DISTRICT (Prospecthouse, Niagara Falls, N. Y., Second Wednesday of Month)

*Oct. 4, 1950:* Visit to the plant of E. I. du Pont de Nemours & Co., Inc., Niagara Falls, N. Y. "Products of the du Pont River Road Plant," by Ross Hare, Manager of the du Pont plant in Niagara Falls.

*Nov. 1, 1950:* "A New Approach to Employee Relations," by F. H. Vaissiere, Shop Training Supervisor, Oswego Falls Corp., Fulton, N. Y. Joint meeting with Niagara Branch, Canadian Paper Association, Technical Section.

*Dec. 6, 1950:* "Some Fundamentals of Coating Methods" by Lawrence W. Egan, Frank W. Egan & Co., Bound Brook, N. J.

*Feb. 7, 1951:* "The General Educational Program of the College of Forestry and Its Research Program," by C. E. Libby, New York State College of Forestry, Syracuse, N. Y.

*March 13, 1951:* (St. Catherines, Ont.) Joint meeting with the Niagara Branch of the C.P.P.A. Technical Section. "International Technical Cooperation," by Lincoln R. Thiesmeyer, Pulp and Paper Research Institute of Canada, Montreal, P. Q.

*April 5, 1951:* "What Are the Problems of the Paper Industry?," by Henry J. Perry, *Paper Trade Journal*, New York, N Y. Election of Officers.

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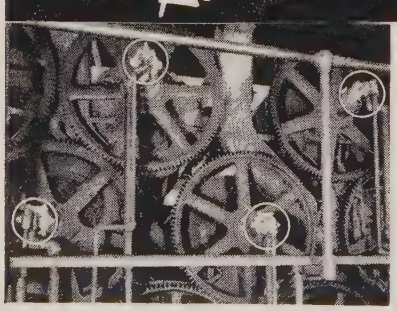

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## *Maine-New Hampshire*

The Maine-New Hampshire Section was organized at Orono, Me., on Oct. 25, 1940, and received its charter at Bangor, Me., on Oct. 26, 1945.

*Oct. 13–14, 1950:* (Keyes Science Building, Colby College, Waterville, Me.) Symposium on "Bleaching of Groundwood Pulp." (1) "Peroxide Bleaching of Groundwood," by J. S. Reichert, E. I. du Pont de Nemours & Co., Inc., Niagara Falls, N. Y.; (2) "Groundwood Bleaching Variables," by F. R. Sheldon, Buffalo Electro-Chemical Co., Inc., Buffalo, N. Y.; (3) "Sulphur Dioxide as a Bleaching Agent," by George V. Rittenhouse, Virginia Smelting Co., W. Norfolk, Va. On Oct. 14 visits were made to the Keyes Fibre Co. mill and the Hollingsworth and Whitney Co. mills at Waterville and Madison.

*June 22–23, 1951:* Visit to Brown Co. mill at Berlin, N. H. (Meeting at Eastern Slopes Inn, North Conway, N. H.) "Effect of Certain Variables on Semichemical Pulping on Pulp Quality," by J. N. McGovern, Forest Products Laboratory, Madison, Wis.; "Ammonia Base in the Neutral Sulphite Semichemical Pulping," by R. M. Jones and T. E. Detecher, The Barrett Division, New York, N. Y.; "Semichemical Pulp Production with Revolving Disc Mills," by C. K. Textor, Bauer Bros. Co., Springfield, Ohio; "Development of a System for Neutral Sulphite Pulping, by Tany Agronin, Shartle Bros. Machine Co., Middletown, Ohio; "Semichemical Pulping with Sprout, Waldron Single Rotary Disc Refiners," by T. W. Small, Sprout, Waldron Co., Inc., Muncy, Pa.

### Industrial Lecture Program at the University of Maine

The Maine-New Hampshire Section has continued to cooperate with the Department of Chemical Engineering at the University of Maine in the prosecution of an industrial lecture program of academic instruction. This marks the third school year that such a program has been in effect at the University of Maine. Although several speakers have participated who represent industries outside of the states of Maine and New Hampshire, the majority of the speakers have been from the pulp and paper mills of these states.

Professor Lyle C. Jenness reports that these courses are well received by the students and that there is definite interest in the continuance of them. The Technology lectures given during the first two years of the program are available in book form from the Lockwood Trade Journal Co., Inc., of New York, entitled "University of Maine Lectures on Pulp and Paper Manufacture."

The program during the last school year consisted of three courses: Pulp Technology, Paper Technology, and Pulp and Paper Mill Equipment.

A tabulation of the speakers and lecture topics follows:

*Pulp Technology*

Fay Hyland, Professor of Botany, University of Maine, "Physical Properties of Wood"; Irwin B. Douglass, Professor of Chemistry, University of Maine, "Chemistry of Cellulose and Wood"; William B. Hilton, Vice-President, Great Northern Paper Co., Bangor, Me., "Woods Operations"; James H. Snyder, Sulphite Superintendent, St. Regis Paper Co., Bucksport, Me., "Wood Room"; H. L. Hayes, Vice-President and General Manager, St. Croix Paper Co., Woodland, Me., "Manufacture of Groundwood—General"; Warren L. Daniell, Superintendent, Bureau of Tests, Great Northern Paper Co., Millinocket, Me., "Manufacture of Groundwood—Grinders"; Marcel Barsalou, Assistant Manager, Sulphite Mill, Edmunston, New Brunswick, Canada, "Sulphite Pulping—Preparation of Sulphur Dioxide"; Oscar E. Anderson, Sulphite Superintendent, International Paper Co., Chisholm, Me., "Sulphite Pulping—Acid Making Systems"; R. N. Miller, Research Department, Oxford Paper Co., Rumford, Me., "Sulphite Pulping—Cooking and Recovery"; John McGovern, Technologist, Forest Products Laboratory, Madison, Wis., "Neutral Sulphite Semichemical Pulping"; Frank Morrison, Assistant Superintendent, Soda Mill, Penobscot Chemical Fibre Co., Great Works, Me., "Soda Pulping"; Forrest W. Brainerd, Staff Technical Director, Scott Paper Co., Chester, Pa.; "Sulphate Pulping"; Vincent P. Owens, Sales Engineer, Combustion Engineering Co., New York, N. Y., "Soda and Sulphate Recovery"; J. S. Reichert, Manager Peroxygen Products Development, E. I. du Pont de Nemours & Co., Inc., Niagara Falls, N. Y., "Peroxide Applications in the Pulp and Paper Industry"; and Elliot Barker, Sulphite Superintendent, Hollingsworth & Whitney Co., Waterville, Me., "Chlorine Bleaching."

*Paper Technology*

John H. Milliken, Director of Personnel Relations, S. D. Warren Co., Cumberland Mills, Me., "Personnel Management"; C. K. Textor, in Charge of Pulp and Paper Div., The Bauer Brothers Co., Springfield, Ohio, "Beating and Refining"; William R. Willets, Paper Development Laboratory, Titanium Pigment Corp., New York, N. Y., "Fillers and Loading"; P. F. Neumann, Manager, Technical Service, Paper Makers Chemical Department, Hercules Powder Co., Wilmington, Del., "Paper Sizing"; E. I. Stearns and F. O. Sundstrom, Calco Chemical Div., American Cyanamid Co., Bound Brook, N. J., "Paper Coloring"; Paul C. Baldwin, Assistant to General Manager of Paper Mills, Scott Paper Co., Chester, Pa., "Paper Machine—Wet End"; W. J. Walker, General Superintendent, St. Regis Paper Co., Bucksport, Me., "Paper Machine—Dry End"; Norman I. Bearse, Vice-President, Champion-International Co., Lawrence, Mass., "Paper Coating"; Charles W. Stillwell, Department Head, Chemical Research, Dennison Manufacturing Co., Framingham, Mass., "Paper Converting"; Joseph King, Technical Service, Eastern Corp., Brewer, Me., "Paper Testing and Specifications"; Robert Graham, The Graham Corp., Boston, Mass., and J. A. Benedetto, D. Benedetto, Inc., New York, N. Y., "Waste Paper—Its Collection and Usage"; A. G. Durgin, Superintendent of Research, Bromption Pulp and Paper Co., Ltd., East Angus, Quebec, Canada, "Special Papers"; and Milton Zucker, Research Manager, International Printing Ink, Elizabeth, N. J., "The Graphic Arts."

*Pulp and Paper Mill Equipment*

E. T. Howard, General Superintendent of Construction, Oxford Paper Co., Rumford, Me., "Pulp and Paper Mill Engineering"; James F. O'Connor, Stanley J. Leen Co., Bangor, Me., "Electric Motors and Controls"; C. L. Durkee, Vice-President and Sales Manager, D. J. Murray Manufacturing Co., Wausau, Wis., "Woodroom Equipment"; P. J. Murdock, Jr., Engineer, Parkman A. Collins Co., Boston, Mass., "Centrifugal Pumps"; F. H. Cole, Manager, Pulp and Paper Mill Div., Walworth Co., New York, N. Y., "Valves and Their Use in the Pulp and Paper Industry"; D. R. Simonds, Engineer, Beloit Iron Works, Beloit, Wis., "Factors Limiting the Speed of Fourdrinier Paper Machines"; Daniel L. Horigan, Engineer, Lukens Steel Co., Boston, Mass., "Stainless Steel: Its Use and Application in the Pulp and Paper Industry"; M. B. Hall, Director of Training, The Foxboro Co., Foxboro, Mass., "Industrial Instrumentation"; E. J. Ward, General Sales Manager, Cameron Machine Co., Brooklyn, N. Y., "The Evolution of Mill Type Slitters, and Roll Winders"; K. J. Mackenzie, Superintendent of Paper Mills, Eastman Kodak Co., Rochester, N. Y., "The Applications of Modern Control Instruments to the Paper Making Process"; S. Jenkins, Jr., Sales Engineer, Bird Machine Co., South Walpole, Mass., "Stock Screening"; G. A. Peterson, Vice-President, Rice Barton Corp., Worcester, Mass., "Dynopulper"; R. T. DePan, Development Engineer, Downingtown Manufacturing Co., Downingtown, Pa., "Pulping and Stock Preparation"; and Harold G. Ingraham, Charles T. Main, Inc., Boston, Mass., "Auxiliary Apparatus Operations Preliminary to Paper Machines."

## *Chicago*

The Chicago Section was organized as the Chicago Professional Paper Group in Chicago, Ill,, in Oct., 1943. In 1946 the Group became the Chicago Section. All meetings are held in the rooms of the Chicago Bar Association on the third Monday of each month.

*Sept. 18, 1950:* Panel Meeting on "Today's Packaging and the Present Emergency." The members of the panel and their subjects were: (1) "Available Materials for Packaging," by Frank Rubinale, Chief of Subsistence Packaging and Packaging Division, U. S. Army Quartermaster Container Institute, Chicago, Ill.; (2) "Packaging Engineering," by Walter Stern, Kraft Foods, Inc.; (3) "Testing and Damage Control," by W. J. Balster, Don L. Quinn Laboratory and Chairman TAPPI Container Testing Committee.

*Oct. 16, 1950:* "Putting the Rainbow to Work" and a motion picture, "Rainbow to Order," by George Welp, International Printing Ink Co., New York, N. Y.

*Nov. 20, 1950:* Panel Meeting—"Corrugated A to Z," F. D. Long, Container Corp. of America, Chicago, Ill., Moderator. Papers: (1) "Theory of the Starch Process for Combining Corrugated Board," by S. F. Thune, National Starch Products, Inc., Chicago, Ill.; (2) "Preventive Maintenance in the Box Shop," by Arthur Sperling, Downing Box Co., Milwaukee, Wis.; (3) "Sodium Silicate as an Adhesive in Corrugated Board Manufacture," by Don Santmyers, Grasselli Div., E. I. du Pont de Nemours & Co., Inc., Chicago, Ill.; (4) "Testing and Quality," by C. J. Zusi, Container Laboratories, Inc., Chicago, Ill.

*Dec. 13, 1950:* Merchants and Manufacturers Club, Merchandise Mart. Annual Ladies Night.


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Bulletin No. 1400 describes the S-P-S Tester as well as other Gurley paper testing instruments. It's worth writing for today. W. & L. E. Gurley, Station Plaza & Fulton Sts., Troy, New York.

*Jan. 15, 1951:* Symposium on "The Growing Shortage of Trained Technical Personnel in the Paper and Pulp Industry." Speakers: Harry F. Lewis, Institute Paper Chemistry, Appleton, Wis.; Alfred H. Nadelman, Western Michigan College, Kalamazoo, Mich.; C. Earl Libby, New York State College of Forestry, Syracuse, N. Y.

*Feb. 19, 1951:* Panel Discussion on "Wartime Packaging." Introduction by Lt. Col. W. R. Crown, Deputy Chief, Chicago Ordnance District: "Ordnance Viewpoints," by M. C. Bilow, Chief of Packaging Section, Chicago Ordnance District; "Plastic Coated Barriers," by L. M. Burgess, H. P. Smith Paper Co., Chicago; and "Greaseproof and Moistureproof Barriers," by Edward Greenman, Midstates Gummed Paper Co., Chicago.

*March 19, 1951:* Symposium on "Current Trends in the Paper Box Industry," Edward C. Berg, Ace Carton Co., Chicago, Moderator. "Boxboard," by Joseph Kubicka, Container Corp. of America, Chicago; "Printing and Cutting," by Harry Wahn, Ace Carton Co., Chicago; "Finishing, Handling, and Production Methods," by John Redpath, Chicago Carton Co., Chicago.

*April 16, 1951:* Panel Meeting on "Raw Materials Supply." "Waste Paper," by James Flett, James Flett Organization, Chicago, Ill.; "Commercial Pulp," by Donald G. Knight, Bulkley Dunton Pulp Co., New York, N. Y.; "Chemicals," by C. W. Peterson, Graselli Chemicals Department, and G. R. Beach, Jr., Electrochemicals Department, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.; "Titanium Pigments," by Arthur A. Coffin, Titanium Pigment Co., Chicago, Ill.

*May 21, 1951:* Panel Meeting on "Corrugated Board Manufacture." Moderator, F. D. Long, Container Corp. of America, Chicago, Ill. Panel Members—C. R. Vander Meulin, Penick & Ford, Ltd., Inc., Cedar Rapids, Iowa; E. M. Hertzmark, Silicate Div., Diamond Alkali Co., Painesville, Ohio; Charles Miehle, Production Superintendent, Eddy Paper Co., Three Rivers Mich. Election of Officers.

## *Lake Erie*

The Lake Erie Papermakers and Converters Association was organized at the Hickory Grille, Cleveland, Ohio, on Oct. 7, 1949. Meetings are held on the third Friday of each month at the Hickory Grille, 929 Chester Ave., Cleveland, Ohio. This organization received its charter as the Lake Erie Section on May 18, 1951.

*Oct. 20, 1950:* "Quality Control," by Howard Coughlin, Thompson Products Co., Cleveland, Ohio. Panel Discussion—Walter Wilks, Chase Bag Co., Chagrin Falls, Ohio; Mike Zales, Great Lakes Box Co., Cleveland, Ohio; A. E. Scharfetter, American Greeting Cark Publishers Co., Cleveland, Ohio; A. W. Cheely, Hankins Container Co., Cleveland, Ohio; L. K. Burnett, Ohio Boxboard Co., Rittman, Ohio .

*Nov. 17, 1950:* "The A B C's of Gravure," by Frank B. Johnson, Intag Div., Interchemical Corp., Cleveland, Ohio; "Gravure Printing from the Press Manufacturer's Viewpoint," by Joseph Martin, The Champlain Co., Cleveland, Ohio.

*Dec. 15, 1950:* Christmas Party.

*Jan. 19, 1951:* "Package Engineering," by Paul Miesslar, Hankins Co., Cleveland, Ohio, and a talk by Capt. G. C. Briant, Commanding Officer, Akron Naval Air Station, Akron, Ohio.

*Feb. 16, 1951:* "How to Reduce Your Materials Handling Costs," by Robert Belt, Merchandising Equipment Executive, American Greeting Card Publishers, Cleveland, Ohio .

*March 16, 1951:* "Wash Reduction in a Paperboard Mill," by Robert C. Sterley, Ohio Boxboard Co., Rittman, Ohio; and "Waste Reduction in Corrugated Plants," by F. D. Long, Container Corp. of America, Chicago, Ill.

*April 20, 1951:* "Surface Treatments," by V. V. Vallandigham, Kelco Co., Chicago, Ill.; "Protective Coatings," by Paul Yoder, Pyroxylin Products, Inc., Chicago, Ill.

*May 18, 1951:* Section sponsored a full-day session of the TAPPI Corrugated Containers Committee on "Corrugated Combining," F. D. Long, Container Corp. of America, Chicago, Ill., Moderator. "Theoretical and Actual Strength Qualities of Corrugated Board," by R. C. McKee and C. Root, Institute of Paper Chemistry, Appleton, Wis.; "Present Operating Problems and Future Hopes of a Corrugated Superintendent," by R. T. Cassady, Vice-President, The Jackson Box Co., Cincinnati, Ohio; "Past, Present, and Future Designs of Corrugated Combiners," by Walter J. Goettsch, Samuel M. Langston Co., Camden, N. J.; "Theoretical Problems of Heating and Drying," by A. E. Montgomery, J. O. Ross Engineering Co., Chicago, Ill. Charter Presentation Ceremonies: L. K. Burnett, Ohio Boxboard Co., Rittman, Ohio, Chairman, Lake Erie Section; Greetings from TAPPI Executive Committee by Richard P. Price, Hammermill Paper Co., Erie, Pa.; "The Establishment of a Local Section," by R. G. Macdonald, Secretary TAPPI, New York, N. Y. Election of Officers.

## *Southeastern Pulp and Paper Society*

*May 14, 1951:* (Hotel Dempsey, Macon, Ga.) First meeting of the Southeastern Pulp and Paper Society. "A Local Section in the Making," by R. G. Macdonald, Secretary-Treasurer, TAPPI, New York, N. Y.; "Expansion Trends in the Pulp and Paper Industry," by G. W. E. Nicholson, Vice-President, Union Bag & Paper Corp., Savannah, Ga.; "The Macon Kraft Co. Mill," Remarks by Herbert A. Kidd, Vice-President, Macon Kraft Co., Macon, Ga.; "As a Meterman Sees It," by S. W. Rose, Chief Meterman, Macon Kraft Co., Macon, Ga.

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P162-51. General Manager. Not over 48 years, for bleached sulphite and the erection of an entirely new bleached kraft mill in eastern Canada.

P163-51. Instructor in pulp and paper technology for a Midwest university.

P164-51. Plant Engineer for book paper mill in Massachusetts.


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P165-51. Production Manager for Midwest mill. Chemical Engineer with about 10 years' experience dealing with fourdrinier paper machines. Age 38–42. Must have good record with labor.

P166-51. Young Engineer for large Wisconsin pulp and paper mill.

P167-51. Chemical Engineer or Chemist. Recent graduate with knowledge of chlorine, caustic soda, and pulp bleaching preferred.

P168-51. Superintendent for fourdrinier mill in Monterrey, Mexico, making all types of kraft papers.

P169-51. Research Director. Career opportunity for Chemical Engineer or Chemist to establish and head up research department responsible for product improvement. Also process development of three paper mills producing kraft and sulphite converted products.

P170-51. Mechanical Engineer to take charge of the repair and maintenance department of a three-machine mill making sulphite and groundwood papers.

### Positions Wanted

E145-51. Chemical Engineer, 36, administrative ability. Experienced in process and quality control, development, and production. Fine paper, specialties, board, and felt. Thorough knowledge of continuous stock refining and control, machine operation, water, and chemical handling.

E146-51. Research Chemist. Ph.D. (M.I.T.) with 18 years' experience in organic chemistry, wood treatment, semichemical pulping of hardwoods, wood laminates, and the preparation, application, and pilot plant manufacture of vinyl resins desires position where this experience and ability to supervise research can be used to full advantage. Publications. Some business training. Now employed near New York but can relocate.

E147-51. Graduate Chemist with B.S. degree from New York State College of Forestry. 15 years' experience as laboratory director and mill control and development supervisor in high-grade rag and wood pulp sheet mill. Wants similar position in new environment.

E148-51. Chemical Engineer with 20 years' technical and management experience, paper coating, coated abrasives, coating and converting machinery, resins, and specialties. Desires technical or production position with established company.

E149-51. Pulp and Paper Engineer, 48, with 16 years' experience in engineering design, development, and construction of pulp and paper mill equipment, process, plant layouts, operations, and maintenance supervision. Specialized in newsprint and book papers. Degrees in Electrical and Mechanical Engineering and Physics with professional license in several states. Presently employed. Desires position as Chief Engineer or Director of Engineering in expanding paper company.

# RECENT BOOKS

**Water, Land, and People.** By Bernard Frank and Anthony Netboy. Alfred A. Knopf, New York, 1950. Cloth, $5^1/_2 \times 8^1/_2$, 329 pages. Illustrated. $4.00.

This book is dedicated to Edward N. Munns, Master Watershed Planner and a principal speaker at the 1949 annual meeting of TAPPI. Mr. Frank is Asst. Chief of the Division of Forest Influences, U. S. Forest Service. It is a presentation of our growing water famines and floods, the human consequences, and the possible remedies. Engineering solutions have been piecemeal to date and inadequate. Even the famous TVA is imperfect because it failed to adopt a watershed approach. In the opinions of the authors, nothing less will do.

Although the book is written in a popular vein for the layman, it presents evidence that is common to any good engineering report. The review is published herein for its industrial implications, but it has a wider appeal to each individual as a citizen since the problem is creeping up slowly and an awareness is necessary to assure water in the future for subsistence and for the outdoor sports.

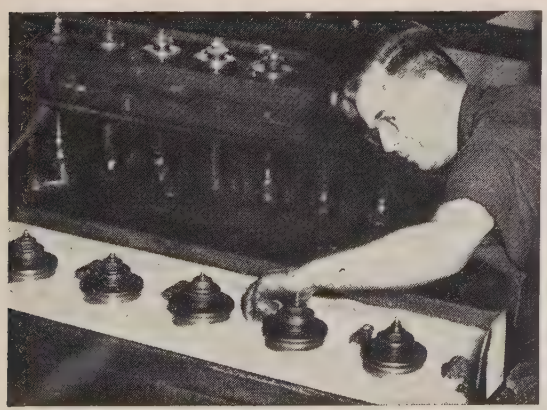
**Organic Reagents for Organic Analysis.** 2nd Ed. By the Staff of Hopkin and Williams Research Laboratory. Chemical Publishing Co., Brooklyn, N. Y., 1950. Cloth, $5^1/_4 \times 8^1/_4$, 263 pages. $5.00.

There is a growing trend in the technical literature for authors to bring together in concise usable form a simplification of the vast amount of heterogenious data that otherwise would require the reader to spend hours and days to locate. This is a commendable service and undoubtedly arises because an author having spent dreary hours bringing such material together for his own use is kind enough to spare his fellow investigators the drudgery of following the same procedure.

The present volume, prepared in Great Britain, is an example of this service. In the first part of the book, the major classes of organic compounds are given, and for each, selected reagents are listed which are best for identifying the class. The second part of the book is a detailed discussion of the selected reagents in alphabetical order. It lists the group of organic compounds for whose identification the reagent is used and describes the method of preparation. In the third part, alphabetical melting point tables of the derivatives discussed in the preceding parts are given.

**Industrial Chemicals.** By W. L. Faith, Corn Products Refining Co., Donald B. Keyes, Heyden Chemical Corp., and Ronald L. Clark, Mellon Institute for Industrial Research. John Wiley & Sons, Inc., New York, 1950. Cloth, 6 × 9, 652 pages. Illustrated. $8.00.

In this book important technical data of manufacture and basic economic facts about 106 major commercial chemicals are given. To each important commercial chemical from acetaldehyde to xylene the following information is given:

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Chester Mankiewicz

Here we show a fine-wire drawing machine being threaded or "strung up." The finished sizes are going through their final drawing in a special lubricant and coolant, then onto spools for use as warp or shute wires.

What began as a one-foot length of heavy wire may "wind up" as a 2,200 foot length of fine 80-mesh wire size.

Expert supervision is employed to control the coolant and to maintain the diamond dies so that they will draw to a tolerance of .0001 inches—another example of the precision required to produce top-quality fourdrinier wires.

**EASTWOOD-NEALLEY CORPORATION • Belleville, N. J.**

Name and chemical formula; flow sheet, manufacturing process and important process variables; equations, for the principal reactions involved and average yield expected in per cent of theoretical yield; raw material requirements per unit of commercial products, including frequently the labor requirements; production chart for past twenty years; generalized use pattern; price chart for twenty years; miscellaneous data, including physical properties, commercial grades, shipping regulations, and usual containers; economic aspects, including historical data; a discussion of competitive products, recent trends in manufacturing and sales; plant size and approximate plant cost; a map showing the location of manufacturing facilities in the United States.

Like many other new books this one has been prepared to save hours of commercial literature research.

**Ion Exchange Resins.** By Robert Kunin and Robert J. Myers, Rohm & Haas Co. John Wiley & Sons, Inc., New York, 1950. Cloth, 6 × 9, 212 pages. Illustrated. $4.75.

This is the first book to assemble and classify the essential information on this increasingly important subject. Mr. Myers is a member of TAPPI and has appeared as a speaker at meetings of the Association.

The book covers the entire field of organic and inorganic exchange materials. Among the subjects covered are the theory and mechanism of ion exchange, cation and anion exchange resin characteristics, the synthesis and application of the resins, water softening and deionizing of water, ion exchange in analytical chemistry, and the design of ion exchange units.

The progress in the field of ion exchange resins has been rather spectacular and has become familiar to the general public in connection with their use in desalting sea water. The present book is a convenient reference book for individuals who may have occasion to deal with applications from time to time.

**Plant Engineering Handbook.** Edited by William Stannier with 87 contributors. McGraw-Hill Book Co., Inc., New York, 1950. Fabricoid, 6 × 9, 1955 pages, 1406 illustrations and 544 tables. $15.

This interesting and valuable book looks very much like the well-known standard engineering handbooks, but a closer study reveals that it is quite different in many respects and is a supplement to such publications. It is written for individuals in industry who are responsible for organization, design, construction, operation, and maintenance. It is a compendium of industrial know-how and deals with the day-by-day problems of industry.

Its major sections cover: Basic industrial costs and cost reduction, foundations, materials of construction, industrial plant fire protection, fundamentals of good plant maintenance, water purification, power plants, instrumentation and control, piping, welding, power distribution and lighting, mechanical power transmission, bearings, lubrication, packings, materials handling, drying, corrosion, waste disposal, heat transfer, graphical mathematics, vibration control, containers and packaging equipment, plastics, patents, and copyrights.

It is quite evident that this volume will join the shelf of essential engineering handbooks in a vast number of plants.

**Chemistry of Industrial Toxicology.** By Hervey B. Elkins, Massachusetts Department of Labor and Industries. John Wiley & Sons, Inc., New York, 1950. Cloth, $5^5/_8 \times 8^5/_8$, 406 pages. $5.50.

This is the first book on toxicology prepared for the engineer and chemist. Emphasis is placed on the industrial poisons themselves and the industrial processes in which they occur, rather than on the physiological effects of poisons on the human body. Nine chapters are devoted to a detailed study of over 200 industrial poisions. The maximum allowable concentrations for 203 substances in air are given. Details of testing are explained.

**Chemical Engineering Cost Estimation.** By Robert S. Aries, Consulting Engineer, and Robert D. Newton, Chas. Pfizer & Co. Chemonomics, Inc., New York, 1950. Paper-bound, $8^1/_2 \times 11$, 109 pages. Lithoprint. $5.00.

This is not a textbook on the subject but rather a handbook that gives quick estimating methods for determining costs by graphical methods of major equipment, piping, insulation, and other auxiliaries. Ratios are presented for the calculation of complete plant, investment, and operating costs.

The graphs and short cuts described will be useful to any manager or engineer planning a new plant. Annual indexes of equipment costs and break-even points are covered.

**Chemical Thermodynamics.** By Frederick D. Rossini, Professor of Chemistry, Carnegie Institute of Technology. John Wiley & Sons, Inc., New York, 1950. Cloth, $5^1/_2 \times 8^1/_2$, 514 pages. $6.00.

This book is aimed to provide instruction for those who have studied physical chemistry and some calculus. Emphasis is placed on the practical application of the laws and principles of thermodynamics to actual physical and chemical systems.

*Note:* Books reviewed in this department may be purchased through *Tappi*, 122 East 42nd Street, New York 17, N. Y.

# Determination of Total Nonaqueous Constituents in Pulp Mill Liquors

J. H. PHILLIPS

RECENT accelerated interest on the part of pulp manufacturers in the recovery of the residual liquors from the several sulphite processes has brought to the foreground the need for more accurate laboratory data for use in establishing accurate material and heat balances in such mills. Such data, needed for comparing efficiency of operation, and heat and chemical balances of the several processes, are dependent to a large extent on the availability of satisfactory and reliable methods of chemical analysis. These methods must be sufficiently sound in principle to give the needed reliability of results, and yet must be developed with the prime considerations of simplicity of procedure and speed of operation foremost in the minds of those charged with the responsibility of applying such methods to daily operation. These same prime considerations have prompted us to give this problem of analytical methods foremost and thorough consideration.

## PRESENTATION OF THE PROBLEM

One of the principal problems confronting operators of sulphite mill recovery processes is that of obtaining a reliable value for the solids content of sulphite liquor. Actually the constituents which make up the so-called "solids" content of this liquor may vary in both chemical form and amount over a rather wide range. It appears somewhat unnecessary to know the exact amount or chemical form of the organic constituents; and the inorganic ash and sulphur contents of such liquors are determined by standard methods. We therefore feel that a better picture of the problem can be obtained first by considering the contents of such liquors from the opposite viewpoint, namely, by the evaluation of the moisture content of the liquor and by grouping all other constituents, whether they be gaseous, liquid, or solid, under the general classification of "total nonaqueous constituents."

A definition of so-called "total solids" of a sulphite liquor must therefore be altered to include those gaseous constituents and easily volatile liquids usually lost in the various drying methods commonly in daily use in many mills. Such a definition might read as follows:

> "The total nonaqueous constituents of a liquor shall, as the term implies, include all constituents either organic or inorganic, present in elemental form or combined in any compounds of any physical state, gaseous, liquid or solid, other than the chemical compound water."

This definition also implies that all water present as combined water, water of hydration, or water of crystallization will be included along with the uncombined water, regardless of physical form, as a part of the aqueous phase of the liquor.

It logically follows that, considering the problem under such a definition, the liquor should no longer be thought of as being divided into two more or less arbitrary fractions, namely, dried residue and volatile matter obtained at an arbitrarily chosen temperature. Neither of these fractions is completely satisfactory in calculating accurate chemical recovery or process efficiency. On the contrary, if a reliable method can be developed for determining the true water content of a liquor thereby separating it from the total nonaqueous constituents a much more usable value would result for application in subsequent engineering calculations.

## REVIEW OF THE LITERATURE

With the above interpretation of the problem in mind, we proceeded to review the literature critically to determine if a method were available from past or current practice that would provide a procedure for quantitatively determining either the water content or the "total nonaqueous constituents" of sulphite liquor samples. In order to cover all possibilities for listing of such a method, technical literature was reviewed under the general classifications of "moisture," "determination of water," and "determination of solids." Since the literature on sulphite liquor netted little desirable information, the same literature classifications for all pulping processes and for a large number of other industrial applications where methods for the determination of moisture or of solids might be applicable were reviewed and are reported here.

### *Methods Used in Other Industries*

*Determination of Solids.* In many instances the basic problem of the industry was entirely different from the one presented here. Often the properties of the sample were sufficiently different to permit application of a different approach to the problem not possible with sulphite liquors. In many instances gaseous constituents or volatile organic compounds either were not present or carried no particular interest to that industrial application.

The most prevalent method for the determination of solids content is some variation of the method of drying the sample at a chosen temperature and specified conditions. For this drying process a variety of types of equipment is described and a variety of materials has been noted which were added to the sample to obtain a more even distribution of heat and a more complete volatilization of materials expelled at the chosen temperature. A few methods were found based on physical properties of the liquid such as density or specific gravity, optical activity, or dielectric constant.

In the food industry a variety of methods are noted. The book, "Methods of Analysis of the Association of Official Agricultural Chemists," 6th Ed. (1945) (*1*), lists methods on several pages, all of which were modifications of the oven-drying technique. These include the use of a variety of material, such as sand, pulverized quartz, and wire gauze, for aid in evenly spreading heat and evenly distributing the sample over a large surface area for fast evaporation. As mentioned previously, these methods are of little value to our particular problem since we are unable to adapt them to a liquor containing volatile organic liquids or gaseous constituents.

Likewise, the "Book of A.S.T.M. Standards" (*2*) provides methods for the determination of solids in industrial water, butadiene, rubber cements, paints, lacquers, and nitrocellulose lacquer and other materials in such standard methods as D 1069–49 T, D 1025–49 T, D 553–42, D 298–49 and D 333–40; however, none of these lend themselves to adaptation to sulphite liquors for the reasons mentioned above.

A variety of types of laboratory equipment and variations of drying ovens have been described in a number of references (*3, 4, 5*).

A reference in a German journal (*6*) provides a method for solids determination of fruits and fruit products similar to methods used on coal which avoid the change in moisture content of the dried material due to exposure to air.

Vacuum drying methods are quite common on materials such as tars, and methods using sulphuric acid as the dehydrating agent in a closed container or special desiccator have worked successfully for food materials and animal feed of various types (*7, 8*).

A method for determining the solid content of ceramic materials was found (*9*). This particular method was a mathematical estimation based on the prerequisite that the solids are insoluble and retain normal physical and chemical properties at all times. Application of such a method was therefore eliminated so far as sulphite liquors were concerned.

*Determination of Water.* A search of the literature on methods for the determination of water or moisture again

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suggested the application of the broad method previously stated which entails driving off the moisture with heat and determining the resultant loss by weighing. One author (*10*) uses alcohol in viscous or semisolid materials to remove the water as an azeotropic mixture. This method gives the total percentage of all substances in the sample which (1) boil below 105°C., (2) form azeotropic mixtures with alcohol which boil below 105°C., (*3*) combine chemically with alcohol to form compounds which boil below 105°C.

Other references discuss methods of distillation consisting of either distilling with a liquid immiscible with water but with a boiling point higher than that of water, or heating with such a liquid and then distilling with another liquid likewise immiscible with water but with a lower boiling point than the first liquid. The methods using such liquids as petroleum or toluene for both the heating and distillation steps or heating with turpentine and distilling with toluene are considered (*11*).

A variation of this method (*12*) makes use of xylene in a distillation apparatus that allows the water to separate from the xylene and automatically returns the xylene to the distilling flask. Similar applications have been made on samples of syrup, molasses, and tar (*12–22*). A similar method was also reported as being used for moisture in sewage sludge (*23*).

The use of toluene as a distilling agent for the determination of water has also been reported (*24, 25, 26*). Another variation specifying the use of toluene as a distilling agent includes the treatment of the distillate with anhydrous copper sulphate which readily combines with the water. The copper sulphate is then filtered off and reweighed and the increase in weight computed as water (*27*).

Similarly, benzine has been used as a distilling liquid (*28, 29*). Other solvents such as kerosene (*30*) and petroleum distillate (*31*) have been reported as well as such solvents as isobutanol (*32*). Heptane has been used for the determination of water, including water of hydration (*33, 34*). A modification of the above methods (*35*) makes use of a centrifuge to effect separation of the water-immiscible layers for accurate determination of the quantity of water distilled.

Such organic liquids as trichlorethylene, methylene chloride, and acetylene tetrachloride have been suggested as compounds to be used with the methods making use of the distillation of azeotropic mixtures (*36–43*). Some of these materials have been used for determining water in fusel oils, alcohols, and mixtures of alcohol with benzine and benzene. Methylene chloride, in particular, forms no azeotropic mixtures with ethyl alcohol or higher alcohols but no mention is made of its behavior with methyl alcohol. Gaseous constituents were of no interest in this particular application so therefore were not mentioned.

Advantages for the use of these methods as well as other distillation methods include:

1. The water is collected and can be examined for purity.
2. Gases and vapors evolved do not affect the results and volatile organic constituents are often dissolved in the liquid other than water.
3. Oxidation and skin formation are avoided.
4. The rate of dehydration is easily shown without removing the sample from the apparatus, as is necessary in the oven-drying procedures.
5. A constant temperature of dehydration can be maintained indefinitely and without trouble.

Unfortunately, these methods do not take into consideration the necessity, from our point of view, of including gaseous components, volatile organic alcohols and acids or azeotropic mixtures of these materials with water, all of which should be included as nonaqueous constituents of the liquor.

Another general method reported for the determination of moisture in various materials includes the use of a chemical having the property of reacting specifically or semispecifically with water. Foremost among those listed was calcium carbide (*44–55*). The use of calcium carbide involves the reaction of water with the carbide liberating acetylene gas. Various means have been devised for the measurement of the gas volume or for reacting the acetylene with other materials such as copper sulphate forming copper acetylide and titrating the copper acetylide with potassium permanganate. Such methods are quick and accurate but acids present in waste liquors also react with calcium carbide to form acetylene and thereby give erroneous answers.

The use of calcium hydride has also been proposed. This material reacts with water to form hydrogen which can be measured (*56*). However, it has been reported (*57*) that ethyl alcohol and acids also react with calcium hydride to yield hydrogen.

The use of magnesium nitride (*58*) has been suggested. The ammonia produced from the hydrolysis of magnesium nitride is distilled from the reaction flask into a measured amount of standard acid and the excess acid is back-titrated. However, if more than 60% methyl alcohol is present the methyl alcohol reacts with the reagent giving erroneous results (*59*). Acids have the same effect as water on magnesium nitride leading to high results.

Methyl magnesium iodide has been used. The interaction of water with the reagent gives methane which can be measured volumetrically (*60, 61*). Since 1 mg. of water liberates 22 ml. of methane, such a method presents the possibility of the use of small samples. Acids and other compounds containing active hydrogen also liberate methane from the reagent.

A method involving the hydrolysis of benzoic anhydride to benzoic acid which in turn is titrated has been reported as another approach to the problem of the determination of water. The method is quite long and complicated entailing heating the sample with benzoic anhydride in a sealed tube for 14 hours at 140°C. followed by a 6-hour refluxing period. This particular method is applicable in the presence of alcohols, aldehydes, and acetals but the presence of acids gives inaccurate results (*62*).

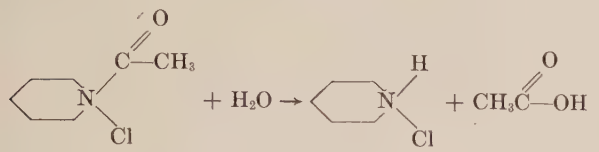
A method making use of the optical activity of a reagent was found for the determination of water in acetic acid (*63*). This method is based on the reaction of the water with a measured excess of acetic anhydride. The excess acetic anhydride is determined by measuring the decrease in optical rotation caused by the decrease in acetic anhydride available to react with d-camphoric acid to form d-camphoric anhydride. This method is quite sensitive but little hope is held for it so far as waste liquors are concerned because of the probability that acetic anhydride would react with other constituents present in the liquor besides water, and because of the opacity of residual liquors which, of course, prevents determination of optical activity. Also, optically active materials, such as some of the types of sugars present in the liquor, would cause erroneous optical measurements.

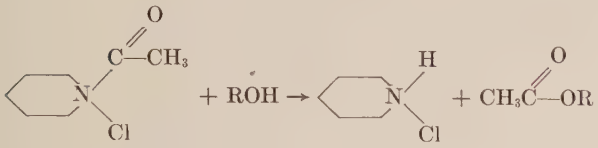
A reference has been found for the use of phosphorous pentoxide as an absorbent for water in a gas mixture (*64*). However, phosphorous pentoxide also reacts with some of the alcohols, ammonia, pyridine, and phenol.

Naphthyl dichlorphosphine oxide has been suggested in two different articles (*65, 66*) and cinnamoyl chloride (*67, 68*) has been used in place of naphthyl dichlorophosphine oxide by others. Consideration of these two compounds has been discarded due to the doubtful end point and the nonstoichiometric qualities of one of the reactions.

The use of a reagent consisting of acetyl chloride and pyridine has been suggested as a titrimetric method for determining water (*69*). This method seems to hold some promise and may be worthy of further investigation at a later date. Acetyl chloride in the presence of pyridine reacts quantitatively with water producing 2 moles of titratable acid. Alcohol reacts similarly, but much more slowly, and produces only 1 mole of acid in the reaction. The reaction with water is so rapid that the presence of a moderate excess of alcohol or

amine will not interfere with the reagent's preferential quantitative reaction with the water. However, the presence of high concentrations of the lower alcohols leads to erroneous results. Equations for the reaction of the acetyl chloride-pyridine reagent or acetyl pyridinium chloride with water and with an alcohol are reported as follows (*71*, p. 14):



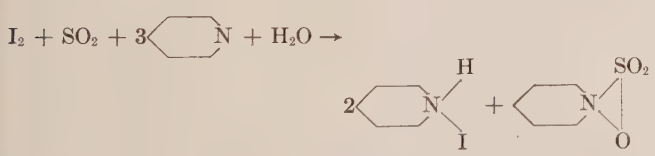


The acids formed by the reaction with water can be titrated without appreciable difficulty or interference from the presence of other compounds. Exceptions to this statement are the interferences by formic acid, methyl alcohol, glycol, and glycerol all of which interfere with accurate water determinations. Other acids react similarly but corrections can be made for their presence by a preliminary titration.

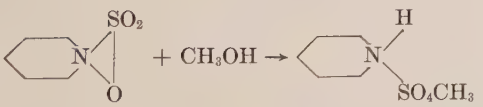
Previous experience with the use of the well-known Karl Fischer reagent has led us to feel that this particular procedure might hold considerable promise for an answer to this problem. This method was developed and first published by Fischer in 1935 (*70*). Since that time numerous papers have been published commenting on the original method, or presenting revisions of that method. A review of a number of these publications has been made as a basis for further work in our laboratory for this specific application.

A recent reference (*71*) indicates the resemblence of the Karl Fischer method to the method mentioned above using acetyl chloride dissolved in pyridine as a reagent. This same reference states that although the original paper on the Fischer method indicated the method was satisfactory for determining water in acetone, these authors were unable to accomplish satisfactory results from that particular titration unless the molar ratios of the constituents of the reagent are altered.

The reagent for the Karl Fischer titration consists of a solution of iodine, sulphur dioxide, and pyridine in methyl alcohol. This reagent reacts with the reduction of iodine to hydrogen iodide as long as any water is present. The appearance of the brown color of iodine in the gold-colored solution mixture determines the end point. The reactions involved in this titration have been reported as follows (*72*):



and



The same authors were able to determine water in alcohols; hydrocarbons, including saturated, ethylenic, and aromatic types; carboxylic acids except formic acid; and esters.

Because of the difficulty of determining the end point in colored substances, Fischer suggested that an electrometric method might be used to advantage for determining the end point. The instrument used to detect the potentiometric end point of the water titration must be sensitive and give a positive reaction with a change of only a few millivolts because the entire change is only 20 millivolts. The time lag also makes it imperative that the first part of the change should be picked up by the detector. The extent of the voltage change need not be recorded as long as it registers the incidence of change. Polarization of the electrodes must be prevented.

A titration apparatus using a Beckman pH meter has been reported (*73*). These same authors ran numerous duplicate and triplicate determinations on a number of sorbitol syrups and process solutions. The volumetric method gave results which showed satisfactory agreement with oven-drying methods but provided more consistent results. Samples used included solutions containing monohydric and polyhydric alcohols, from methanol through the glycols, and glycerol to sorbitol and mannitol. Titration values agreed well with calculated values and results were obtained in 5 minutes as contrasted to the 24 to 28 hours often needed for oven-drying methods. The electrodes used were platinum and tungsten.

Still another group of workers (*74*) improved on the apparatus described above using a dead-stop end point modification. This depended on the fact that when an electromotive force of 10 to 15 millivolts is impressed upon two platinum electrodes immersed in the Fischer reagent, sufficient current flows through the solution to deflect a galvanometer off the scale. During the titration of the Karl Fischer reagent with a standard solution of water in methanol, the galvanometer remains deflected until the end point is approached. Near the end point, the galvanometer is affected by each addition of the water solution, and at the end point the galvanometer suddenly comes to a steady reading near its rest point. The dead-stop apparatus is continuous reading, and requires practically no adjustment from day to day, while the potentiometric apparatus must be adjusted before each individual titration. The dead-stop method gives a sharp and reproducible end point in nonaqueous solutions with fewer manipulation difficulties than the potentiometric method and better precision than the visual method, according to the above authors.

Other workers (*75*) have developed a general method for determining moisture in such widely differing materials as grained gunpowder, glacial acetic acid, sawdust, and shellac solutions. An electric unit combining an end point indicator, cell, and electrode system was devised and described. The method is applicable to high- or low-range moisture content and to opaque and colored solutions such as shellac.

Sodium acetate trihydrate has also been suggested as a standardizing agent for the Fischer reagent (*76*). Sodium acetate is quite pure, not hygroscopic and is extremely soluble in the Fischer reagent. An exact sample can easily be weighed for standardization purposes. In our laboratory we have not found this material to be a satisfactory standard.

Another variation (*77*) of the electrometric titration procedure used a 2-volt cell as the source of potential and a high resistance of 3000 to 10,000 ohms in the circuit. The shunt resistance was from 2.5 to 10% of the galvanometer resistance. Initially, in the methyl alcohol solution, the calculated potential applied was 1 to 2 volts, but at the end, only about 0.15 volt. In the titration as carried out in this instance, the Fischer reagent is added in 0.2-ml. portions until near the end point and then the reagent is added dropwise. The end point lasts about 10 seconds; after that, absorption of water from the atmosphere interferes. Duplicate determinations having an average deviation from the mean of 0.5% can be obtained.

An all-glass modification of a previous apparatus has been reported (*78*); and other authors (*79*) modified the procedure to give a sharp clear image in an electric eye when the end point is reached. The precision obtained by these modifications is said to be about the order of magnitude of that of a simple acid-base titration.

Probably one of the most helpful improvements in the

method is that of splitting the reagents into two solutions so that neither solution is destroyed by the presence of moisture vapor in the surrounding air. This particular improvement therefore eliminates the necessity for special glass apparatus and the need for a number of special techniques formerly developed to prevent either the sample or the reagents from absorbing moisture from the air during titration. This particular improvement has been reported by one author (*80*) and rechecked by a group the following year (*81*). This first author, Johansson, prepared the two reagents in the following manner. Solution 1 consisted of a weighed amount of $SO_2$ dissolved in a specified mixture of pyridine and anhydrous methyl alcohol. Solution 2 was made by dissolving a weighed quantity of iodine in anhydrous methyl alcohol. Approximately 15 ml. of solution 1 was titrated with solution 2 to an end point determined either visually or electrometrically. This titration provided a correction for the water content of the reagents. The sample was then added to this mixture and the titration was again carried out by adding solution 2 previously standardized against a known weight of water.

This same author, making use of the two-solution reagent, reported the determination of water in various samples of pulp and rayon, methyl alcohol, ethyl alcohol, sugar solutions, tall oil products, and similar substances. Dark-colored liquids such as black liquors, in which the color change with the addition of excess iodine cannot be observed, can be titrated electrometrically with platinum electrodes. Iodine consumption corrections can be made by this method to eliminate the effect of the unsaturated compounds usually present in black liquors. This article is the only reference found on the application of the Karl Fischer reagent to paper liquors of any kind and Johansson reported only one sample of evaporated black liquor. These data indicated very little experimental work and no direct application to the industry.

Our own work on developing a method primarily for sulphite liquors but no doubt usable on other types, has been an adaptation of this divided reagent method. This work will be described in detail later in this paper.

The second authors (*81*) verified the above procedure and proved it was stoichiometrically correct. They reported an equation for the reaction taking place during standardization of solution 2 with water as given below and proved the reaction was 99.5% stoichiometric.

$$H_2O + SO_2 + I_2 \rightarrow SO_3 + 2HI$$

The Karl Fischer reagent, although not referred to as such, was described (*82*) and used with a direct electrometric titration of the sample. A solution of iodine and $SO_2$ gas in a mixture of absolute alcohol and pyridine was used with polarizing electrodes and an optical indicator for registering changes in current strength during the titration. The particular electrode used raised the sensitivity of the apparatus two to three times, and optimum selection of resistances gave it greater stability.

Other references applying the use of Karl Fischer reagent to foods (*83*), and to formic acid (*84*), were found. Previously the reagent was not recommended for determining water in formic acid because of the dehydration of the acid; however, the authors indicated in the latter reference that under normal conditions this interference is not appreciable.

An indication of the growing popularity for application of this particular reagent to problems involving the determination of water is indicated by two references found in 1951 journals so far. The first, a reference in the Jan. 1951 issue of *Analytical Chemistry* (*85*), reports considerable improvement in the visual method of titration with Karl Fischer reagent by the use of a yellow light for viewing the end point. This no doubt aids considerably in the ease of titration where visual end points are used. However, with sulphite liquors such a titration is not possible and one of the electrometric methods proved to be much more applicable to our problem. The second reference referred to above is one which appeared in the Jan. 22, 1951, issue of *Chemical & Engineering News* (*86*). This article, containing a report of the January 8th meeting of the North Jersey Section of the American Chemical Society, included a short description of a new automatic titration apparatus for carrying out the Karl Fischer titration. This apparatus is equipped with a precision ultrasensitive relay and a timer which actuates a magnetically operated all-glass solenoid valve to give extreme accuracy even with solid samples suspended in the solvent. This instrument makes use of the potentiometric titration procedure so that simple titrations can be completed in 15 to 30 seconds, and difficult titrations can be done in 1 to 3 minutes with a high degree of precision. The timer relay in the apparatus times the duration of the end point and stops the titration only when the true end point is reached. For those interested in special automatic equipment this instrument may have some merit in our specific application.

A few of the advantages found for the Karl Fischer reagent method are as follows:

1. The method is extremely rapid.
2. Good precision and reproducibility are claimed in practically all references.
3. Samples containing an extremely wide range of water content can be handled by the same method. Samples containing water as a major constituent require a considerably larger volume of reagent, or slight revisions of technique or procedure.
4. The determination may be carried out in colored solutions by means of electrometric titrations.
5. Gaseous constituents and most volatile liquids have no effect on the reagent.
6. The method should give water of crystallization or water of hydration in addition to the water present in an uncombined state.

Substances which have been satisfactorily analyzed for their water content by the Karl Fischer method include ethylene and propylene glycols, glycerol, oxalic and oleic acid, sulphosalicylic acid, methanol, ethanol, glucose, galactose, maltose, lactose, sorbitol, cotton, undefibrated and defibrated wood pulp, tall oils, aqueous hydrogen peroxide solution, organic peroxides of the dialkyl type, certain sulphur compounds including mercaptans, starch, dextrose, polyvinyl alcohol, cellulose derivatives, pectin, crushed oil seed cake, and a variety of inorganic salts and their solutions (*87*, *80*, *71*). This list of materials includes almost everything that might be expected to be present in residual liquors. This fact gave considerable support to our original idea of attempting to adapt the Karl Fischer reagent to residual liquor analysis.

Disadvantages which have been found listed for the Karl Fischer reagent include:

1. Solutions containing unsaturated compounds react with iodine in the "one solution reagent" giving erroneous titrations.
2. Elaborate equipment providing completely anhydrous conditions for the titration are necessary where the "one solution" method of titration is used.
3. Strongly alkaline substances, for instance, soaps, soda, sodium phosphates, perborates, ammonia, organic peroxides of the diacyl type, active aldehydes, and similar materials cannot be analyzed by this method because of interference due to various side reactions with the reagent.

As indicated above, disadvantages 1 and 2 can be overcome by the use of the "two solution reagent" method. Active aldehydes are not expected to be present in sulphite liquors due to the presence of acetic acid and $SO_2$. However, if interference is experienced from the presence of these materials they can be eliminated by treating the sample with hydrogen cyanide (*71* p. 151, *88*).

Numerous physical methods have been devised for determination of water. One method was described for determining moisture in synthetic rubber condensate and high boiling alcohols by the addition of potassium fluoride either

as a saturated solution or an ignited salt (*89*). The water phase separates from the other materials as an immiscible layer.

Benzene has also been used as a fractional extraction reagent for material such as acetone oils (*90*).

Application of phase rule diagrams to this same problem have been reported in at least two different papers (*91*, *92*). A substance insoluble in water such as a hydrocarbon or benzene is added to the sample and the temperature at which separation takes place is found. By reference to a curve of known concentrations, the percentage of water content can then be determined. A slight variation of this same procedure is the determination of the temperature at which turbidity appears (*93*) or the determination of the quantity of benzene needed to produce turbidity with reference to a curve of known percentages. Centrifugation in a graduated tube has also been used for separating water in the presence of benzene or gasoline as a separating reagent (*94*, *95*).

A unique method which provided the inventors a British patent (*96*) consists of blowing dry air across the sample, evaporating the moisture from the sample by this method, and passing the air across wet and dry bulb thermometers. The difference in temperature between the two thermometers is recorded and reference to a previously constructed calibration curve provides the percentage of moisture present.

Numerous references were found based on the application of a measurement of the dielectric constant or other similar electrical measurements (*97–103*).

Numerous reviews of various methods of moisture determinations have been found in the literature. One group of authors discuss all methods of water determination except water in gases (*104*). The advantages and disadvantages of the various methods were presented. One author gives a general review (*105*) for moisture determinations and another (*106*) discusses the errors of drying methods and of alcohol extraction plus drying methods. Still another author (*107*) gives a review of electrical methods for water determinations.

### *Methods Used in the Pulp and Paper Industry*

A review of the literature on methods used by the pulp and paper industry for the determination of solids in waste liquors revealed publications on investigations of this problem as early as 1913 (*108*) and possibly earlier. Since that time a variety of methods have been tried, including: (1) oven-drying methods, with and without prior neutralization or the use of heat-distributing material such as sand or quartz pieces; (2) solvent extraction methods; (3) distillation methods, with and without previous neutralization of the organic acids present; (4) various desiccation methods; and (5) combinations of these.

One variation of the drying method (*109*) reported was the use of blotting paper as a means of spreading the liquor for more thorough and rapid evaporation. This method was used on a sulphate mill evaporator feed liquor, and the sample on the blotting paper was dried for 15 minutes at 230°F. Results obtained by this method compared favorably with those obtained by a procedure of xylene extraction followed by drying overnight in an oven. Another variation of the oven-drying method (*110*) included a procedure for neutralizing the volatile acid components in the liquor before evaporation to dryness. These acids include organic acids such as acetic and formic, sulphurous acid, and free sulphur dioxide, and were neutralized by the addition of a previously determined amount of sodium hydroxide solution. Following neutralization of the liquor to a pH of 8.5 to 9, the liquor was evaporated to dryness at a constant temperature of 105°C. This neutralization method prevented loss of gaseous sulphur dioxide and volatile acids present. Other volatile organic compounds present originally or formed by decomposition of the liquor during drying were not retained.

Other authors (*111*) have specified, apparently for the first time, the use of a stoppered weighing bottle and the drying of sulphite liquor at 105°C. for 24 hours as a means of total solids determination. After drying, the weighing bottle is cooled in a desiccator.

A publication from the Pulp and Paper Institute of Canada revealed that several methods were tested in an attempt to standardize on a method for solids determination (*112*). In a discussion concerning obtaining a sample by volume measurement, it was pointed out that these liquors do not drain from a pipet in the same fashion that water drains, and that sampling errors can be introduced because of this particular difficulty. Their chosen method of drying was essentially that of the preceding reference including a standardization of drying at 103 to 105°C. for 24 hours in an oven with air circulation. An attempt was made to prevent oxidation and carbonization, the first of which gives higher results and the second, lower results than the correct answer. It was felt that a standardization of procedure would avoid fluctuations due to these two difficulties.

The volume of TAPPI Standards on Testing Methods (*113*) lists tests T 625 m-48 and T 629 m-48 for the analysis of sulphate black liquor and sulphite waste liquor respectively. These methods specified for determining total solids entail evaporating and drying a sample in an ignited and weighed crucible at 105°C. for 24 hours. This procedure is quite similar to those described above.

Japanese chemists reported work on both calcium bisulphite and magnesium bisulphite liquors. A trial of several methods was made and results reported (*114*).

A number of variations of distillation techniques have been reported. One of these (*115*) was the use of chloramine to oxidize the sulphur dioxide in solution preceding a distillation procedure. The volatile organic acids obtained from this distillation were then titrated with tenth normal sodium hydroxide and calculated as acetic acid.

An ether extraction method was proposed (*108*) and, with slight modifications (*115*), reported as giving results which were in good agreement with the distillation method using chloramine. An exception to this agreement was found in liquors with high free-acid content. With such liquors the distillation method gave a high comparative value due to the formation during distillation of organic acids not originally present in liquor. Titration of the original liquor with aqueous barium hydroxide solution prior to distillation overcame this difficulty.

## REVIEW OF UNPUBLISHED WORK

A search through our own files indicated that our work started on this problem in the early 1930's and since that time we have tried a variety of methods including several variations of the oven drying method, the distillation methods, and the solvent extraction methods with a variety of solvents.

One of the distillation methods tried in our laboratory was fractional distillation in a partial vacuum with the tip of the condenser immersed in a solution of sodium hydroxide. A method of solvent extraction and subsequent distillation using a variation of the apparatus devised by Dean and Stark for the determination of water in oil (*116*) was tried. Such solvents as xylene, trichlorethylene, and other similar ones were tried, but very little success was experienced with this method.

Private communications with a number of pulp manufacturers indicate that considerable cooperative efforts have been exerted on this problem with a number of the interested companies during the past several years. Despite this continued effort by several laboratories, the same objections seem to appear repeatedly in the files. These may be summarized as follows:

1. Oven-drying methods provide a value which does not include, as part of the "total solids," all volatile liquids and gaseous constituents present in some types of liquors.

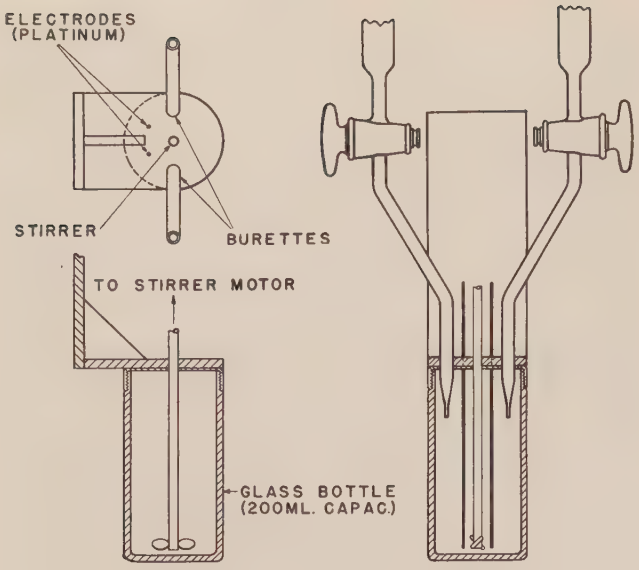



*Fig. 1. Titration assembly*

In many instances, difficulty has been experienced due to foaming, or due to the formation of a scum over the liquor which hinders thorough drying of the sample and makes it impractical to obtain a final weight.

2. Distillation methods result in the loss of gaseous constituents and necessitate a rather complete analysis of the distillate in order to separate the water content from other volatile materials. Degradation of a number of the organic compounds during distillation of the liquor has also resulted in obtaining a variation in quantity of volatile organic material in the distillate. No completely satisfactory and reliable technique could be found to collect and retain all of the volatile constituents, particularly gaseous compounds, alcohols, esters, and ketones.
3. Various methods for neutralization of the organic acids in these constituents prior to drying or distillation have been reported. Various materials such as sand or powdered quartz have also been tried at different times as additives to the evaporating dish or distillation flask. Oxidizing agents have been added prior to evaporation or distillation. None of these have overcome all the difficulties.
4. Solvent extraction methods using a variety of solvents and types of equipment have been tried. These methods have provided various degrees of satisfaction depending somewhat on the liquors involved as well as on the solvent and apparatus used, but have not satisfied the industrial need.
5. Various drying agents have been used in desiccators with the usual objection of the formation of a skin over the liquor and hence a lack of complete drying of the sample.
6. Various hydrometer calibrations have been attempted but a reliable method for obtaining the basic data necessary for the calibration of the hydrometer is lacking. Given such a method, the hydrometer may eventually prove to be a desirable control instrument.

## EXPERIMENTAL DEVELOPMENTS

After thoroughly considering the various methods found in the literature reported above, and after a thorough review of our own files including the intermittent testing program we have been conducting for the past several years, we have come to the conclusion that a modification and adaptation of the well-known Karl Fischer reagent would probably be most universally applicable and give the most exact values for the water content of liquor samples. It is realized that there are a number of questionable factors in the use of this particular method. Although no references were found reporting the extensive adaptation of this procedure to the variety of pulping liquors available, this particular reagent has been applied individually to practically all of the chemical constituents that might be found in pulping liquors. Undoubtedly mixtures of constituents will occur in the various pulping liquors to be considered that will require minor variations of the procedure presented here. It is for the reasons mentioned above that this method is not to be taken as a final and unquestionable procedure in its present form; rather, it is being offered to the industry as a method which, we believe, will be adaptable to the determination of water in almost any type of pulping liquor. Time has not permitted us to examine exhaustively all of the various possibilities, but, considering those which we have examined, we are considerably encouraged by the results obtained.

Our modification is no doubt not in its final form, but it is described in the following paragraphs as we are currently using it.

### *Methods of Analysis*

*Reagents and Solutions.* Solution 1: Prepare by bubbling 60 g. of sulphur dioxide into a mixture of 300 ml. of anhydrous methanol and 300 ml. of dry pyridine. The desired amount of sulphur dioxide to be dissolved in the solution can be measured by determining the increase in weight of the reagent as the gas is bubbled into it.

Use anhydrous methanol and pyridine to eliminate the water in the solvent. Store the solution in a glass-stoppered bottle to minimize moisture pickup from the air. Since the freshly made solution gives erratic results, storage overnight before using seems necessary.

Solution 2: Prepare by dissolving approximately 60 g. of iodine in a liter of absolute methanol. The concentration of this solution may be varied for convenience depending on the average water content of the unknown samples and the preference of the operator.

The strength of this solution is expressed as milliliter equivalents of water. We have found that a solution which has an equivalent strength of about 3 mg. of water per ml. of iodine solution requires 60 g. of iodine per liter. More concentrated solutions will permit the use of larger samples.

*Equipment.* Equipment required includes a titration assembly which provides for two accurately calibrated burets for introducing the two reagents, and an end point detecting assembly consisting of a dry cell, a variable resistance, a galvanometer, and two platinum electrodes.

Figure 1 shows a plan view and side and front elevation of the titration assembly which are self-explanatory. The framework is made of sheet Plexiglas which, in turn, is fastened to the titration stand. The bottle is a standard wide-mouth, screw-cap bottle with the lid fastened to the Plexiglas and drilled to accommodate two buret tips, two platinum wire electrodes, and the glass stirrer.

Figure 2 shows the wiring diagram of the end point detecting assembly.

*End Point Determinations.* Add 15 ml. of solution 1 to the titration bottle, start the stirrer motor, and adjust the

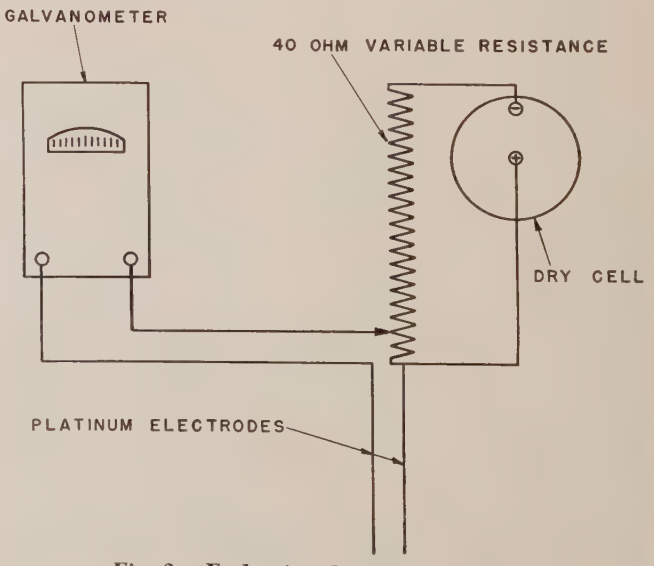



*Fig. 2. End point detecting assembly*

**Table I. Per Cent Water in Evaporated Magnesium Bisulphite Liquor (By the Modified Karl Fischer Method)**

| *Sample no.* | $H_2O$, % | *Deviation from average* |
|---|---|---|
| 1 | 48.9 | 0.0 |
| 2 | 49.4 | +0.5 |
| 3 | 48.8 | −0.1 |
| 4 | 48.9 | 0.0 |
| 5 | 49.4 | +0.5 |
| 6 | 48.6 | −0.3 |
| 7 | 48.7 | −0.2 |
| 8 | 48.5 | −0.4 |
| 9 | 48.9 | 0.0 |
| 10 | 49.0 | +0.1 |
| 11 | 49.3 | +0.4 |
| 12 | 48.7 | −0.2 |
| 13 | 48.8 | −0.1 |
| 14 | 49.0 | +0.1 |
| 15 | 49.0 | +0.1 |
| Av. = | 48.9 | |

variable resistance so that the potential between the platinum electrodes produces a deflection of 1 scale division on the galvanometer. Titrate by adding solution 2 from a buret. As the end point is approached, the galvanometer needle starts to swing, and at the end point maximum deflection is obtained. To check for a true end point, turn off the stirrer motor. If the end point is a true one, the needle slowly drifts back to minimum deflection and rises to maximum deflection when the stirrer motor is again started. If the end point is exceeded, the needle remains steady at maximum deflection when the stirrer motor is turned off.

*Standardization of Reagents.* Since it is impossible to store these reagents for extended lengths of time without moisture pickup, it is necessary to standardize solution 2 each day before starting titrations on unknown samples. Standardization is completed as follows: To approximately 15 ml. of solution 1 in the titration bottle, add solution 2 from a buret, 1 ml. at a time, until the end point is approached, then add dropwise until the galvanometer indicates the end point, and record the volume of solution 2 required. Add an accurately weighed amount of water, approximately 50 mg., determined as described below, to the solutions in the titration bottle and continue the addition of solution 2 until a second end point is obtained. Record the volume of solution 2 used in the second titration. Calculate the titer of solution 2 from the volume used for the second titration.

Determine the weight of the water sample mentioned above by weighing a dropping bottle containing a quantity of water, transfer an approximate amount of water from the dropping bottle to the titration assembly with the dropper and again reweigh the dropping bottle and contents. The difference in the first and second weights of this dropping bottle will provide the sample weight. For convenience, instead of weighing the water directly, a measured quantity of methanol or ethanol with a known water content may be used as a standard.

*Determination of Iodine Equivalent of the Unknown Material.* Since it is possible that side reactions will occur in many of these waste liquors it is necessary to determine the iodine equivalent of these liquors in advance so that the amount of iodine consumed in these side reactions can be subtracted from the total titration volume to provide a measure of the true water content of the liquor.

Transfer an exactly weighed sample of the liquor to the cleaned titration bottle and dilute it with approximately 15 ml. of anhydrous methanol. Omit the use of solution 1, but proceed with the titration with solution 2 in the usual fashion to the desired end point. The volume of iodine solution used in this titration is the measure of the iodine consumption of the sample. The volume of solution 2 divided by the sample weight gives the iodine equivalent per gram of sample. This equivalent multiplied by the weight of the sample used in an

**Table II. Per Cent Volatile Material in Evaporated Magnesium Bisulphite Liquor (By Oven Drying, 24 Hr. at 105°C.)**

| *Sample no.* | *Loss in weight, %* | *Deviation from average* |
|---|---|---|
| 1 | 51.1 | +0.1 |
| 2 | 51.0 | 0.0 |
| 3 | 50.9 | −0.1 |
| 4 | 51.3 | +0.3 |
| 5 | 51.0 | 0.0 |
| 6 | 50.9 | −0.1 |
| Av. = | 51.0 | |

actual water titration will give the volume of solution 2 which should be deducted from the buret reading during titration for water in the sample.

*Titration of Unknown Sample.* Measure 15 ml. of solution 1 into the clean, dry titration bottle, titrate to an end point with solution 2 and record the volume of solution 2 used. Thoroughly shake the unknown liquor sample, transfer a small portion of that liquor into a weighing bottle stoppered with a medicine dropper. Weigh the dropper bottle and contents accurately and transfer the desired portion of liquor from the weighing bottle to the titration assembly and reagent mixture mentioned above. Reweigh the dropper bottle accurately and obtain the sample weight by the difference between the first and second weights. Proceed with the titration of the unknown solution by the addition of solution 2 from the buret to the desired end point.

The volume of solution 2 needed for the second titration represents the sum of the volume needed for the water in the sample plus the volume needed for the iodine consumption of the sample. Obtain the volume consumed by the water by subtracting from this total volume a calculated volume equivalent to the iodine consumption by side reactions as previously determined. The water content of the unknown liquor can be determined by the following equation:

$$\frac{\text{Corrected ml. solution 2} \times \text{water equivalent of solution 2} \times 100}{\text{Sample weight in grams}} = \% \text{ water}$$

The per cent of "total nonaqueous constituents" in the sample is 100 − % water.

### *Discussion of Results*

Table I provides an evaluation of reproducibility of the method on evaporated magnesium bisulphite liquor. The average weight of samples used in these determinations was 0.15 g. while the average sample weight for the oven-drying method was 7.0 g. The deviations from the average shown in Table I are numerically larger than the deviations obtained for the oven-drying method but we feel that this is due entirely to the extremely small size of the sample and are taking steps to revise the procedure still further to permit the use of a larger liquor weight.

**Table III. Per Cent Water in Weak Magnesium Bisulphite Liquor (By the Modified Karl Fischer Method)**

| *Sample no.* | $H_2O$, % | *Deviation from average* |
|---|---|---|
| 1 | 84.6 | −0.6 |
| 2 | 85.3 | +0.1 |
| 3 | 85.6 | +0.4 |
| 4 | 85.1 | −0.1 |
| 5 | 84.5 | −0.7 |
| 6 | 86.1 | +0.9 |
| 7 | 85.7 | +0.5 |
| 8 | 85.3 | +0.1 |
| 9 | 84.9 | −0.3 |
| 10 | 85.6 | +0.4 |
| 11 | 84.6 | −0.6 |
| 12 | 85.3 | +0.1 |
| 13 | 85.5 | +0.3 |
| 14 | 85.0 | −0.2 |
| Av. = | 85.2 | |

**Table IV. Per Cent Volatile Material in Weak Magnesium Bisulphite Liquor (By Oven Drying, 24 Hr. at 105°C.)**

| Sample no. | Loss in weight, % | Deviation from average |
|---|---|---|
| 1 | 85.1 | 0.0 |
| 2 | 85.2 | +0.1 |
| 3 | 85.3 | +0.2 |
| 4 | 85.3 | +0.2 |
| 5 | 85.1 | 0.0 |
| 6 | 85.1 | 0.0 |
| 7 | 85.3 | +0.2 |
| 8 | 84.9 | −0.2 |
| 9 | 85.2 | +0.1 |
| 10 | 84.9 | −0.2 |
| Av. = | 85.1 | |

In addition to the reproducibility of the method as such, it should also be pointed out that samples 1 to 4, 5 to 8, and 9 to 15 each represent a different portion transferred from the bulk sample to the weighing bottle. This, therefore, indicates that the method for sampling the bulk container of waste liquor was also satisfactory.

Table II shows a tabulation of the per cent loss in weight, and deviations from the average, using an oven-drying method for a series of six samples identical to those reported in Table I.

It will be noted that the loss of weight (or moisture) values obtained by the oven-drying method on evaporated magnesium base liquor are approximately 2% higher than those obtained by our titration procedure. We feel that this is a reasonable difference in view of the possible decomposition of the organic constituents during drying of the sample. It is a well-known fact, reported several times in the literature, that carbonization of the sample will give low residual solids values. Some of the compounds in sulphite liquors will quite likely decompose at temperatures used in the oven-drying procedure.

This same difference in results probably exists in samples of weak liquor but is not as detectable because the ratio of volatile gases and liquids to water in the sample is much less in the weak liquors than in the evaporated liquors. This fact would tend to minimize any difference in water content as shown by comparing titration values with the loss in weight by the oven-drying procedure. Table III shows a series of values obtained by titration of weak liquor from the magnesium bisulphite process with Karl Fischer reagent. Table IV gives values of loss in weight using the oven-drying method on a series of identical samples. Samples reported in Table III averaged 0.09 g. in weight, compared to 5.3 g. average for those contained in Table IV.

The first nine samples in Table III were titrated using one batch of solution 2 and the remainder of that table are determinations obtained from the use of a second batch of solution 2. This, of course, indicates satisfactory reproducibility of results with subsequent batches of reagent and subsequent standardizations. Reliability of the sampling technique is again indicated by the fact that samples 1 to 6, 7 to 9, and 10 to 14 each represent separate portions of the bulk liquor sample.

Table V shows results obtained on weak calcium bisulphite liquor samples by the titration procedure. Samples 1 to 6 and 7 to 10 represent separate portions of the bulk liquor sample. The average sample weight was 0.17 g. compared to 5.2 g. for samples used in the oven-drying method.

**Table V. Per Cent Water in Weak Calcium Bisulphite Liquor (By the Karl Fischer Method)**

| Sample no. | $H_2O$, % | Deviation from average |
|---|---|---|
| 1 | 86.2 | 0.0 |
| 2 | 85.8 | −0.4 |
| 3 | 86.3 | +0.1 |
| 4 | 86.4 | +0.2 |
| 5 | 86.2 | 0.0 |
| 6 | 85.8 | −0.4 |
| 7 | 86.2 | 0.0 |
| 8 | 86.6 | +0.4 |
| 9 | 86.3 | +0.1 |
| Av. = | 86.2 | |

**Table VI. Per Cent Volatile Material in Weak Calcium Bisulphite Liquor (By Oven Drying, 24 Hr. at 105°C.)**

| Sample no. | $H_2O$, % | Deviation from average |
|---|---|---|
| 1 | 87.2 | 0.0 |
| 2 | 87.2 | 0.0 |
| 3 | 87.3 | +0.1 |
| 4 | 87.2 | 0.0 |
| 5 | 87.1 | −0.1 |
| 6 | 87.3 | +0.1 |
| 7 | 87.1 | −0.1 |
| 8 | 87.3 | +0.1 |
| 9 | 87.2 | 0.0 |
| 10 | 87.3 | +0.1 |
| 11 | 87.2 | 0.0 |
| Av. = | 87.2 | |

Table VI shows values of per cent loss in weight obtained on a series of samples identical to those used for the titration reported in Table V. Here again, it will be noted that the loss in weight by the oven-drying method is approximately 1% greater than the per cent water found by titration. This difference in values is considered reasonable due to loss of volatile organic compounds and gases. These samples of weak calcium base liquor show the difference in results obtained by titration and by oven drying on this weak calcium liquor sample is more pronounced than with weak magnesium liquors; however, we have not had an opportunity to determine the significance of this point.

It should be reported that difficulty has been experienced in the titration of the evaporated calcium liquors due to the formation of a gummy mass on the bottom of the titration bottle upon addition of the sample to solution 1. There has been insufficient time to investigate completely this phase of the problem, either from the viewpoint of reliability of the titration with this mass present or for the purpose of eliminating its formation. It may be worth while to note, however, that although all the samples used for the titration reported in Table V were less than 0.22 g. of liquor, it was noticed that the largest of these samples showed indication of a precipitate formation. No unusual deviations from the average percentage were found during the titration, however.

Although data reported in this paper cover only magnesium and calcium liquors from the sulphite process, we feel confident that the method will be equally satisfactory for almost all other types of waste pulping liquors encountered. As we have indicated previously, almost all that are likely to be present in any pulping liquor have been encountered individually by other investigators and methods are provided in our revised procedure for eliminating interference expected from such materials as unsaturated compounds possibly present in black liquor.

Also, as we have indicated previously, we want to again emphasize that this presentation should be accepted as a progress report, presented to the industry to give other investigators the benefit of our experience to date. Although we feel certain that the principles comprising this particular method are sound in every respect, we have not had sufficient opportunity to weed out all possible interfering factors and minor revisions may be desirable in certain specific instances. Because of these facts, we are continuing our study of this problem in our own laboratory and expect to report this more extensive study as soon as it is completed.

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Received Feb. 23, 1951. Presented at the Annual meeting of the Technical Association of the Pulp and Paper Industry, New York, N. Y., Feb. 19–22, 1951.

The author wishes to express his appreciation to M. M. Rubright, Assistant Chemist; R. V. Cobb, Senior Chemical Engineer; and C. E. Rogers, Research Engineer for valued assistance in development of the problem and preparation of this manuscript. Mr. Rubright should be given full credit for a major portion of the literature search and the actual laboratory testing done toward adaptation of the Karl Fischer reagent to this particular application.

# The Requirements of Coated Papers for Offset Lithography

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Many of us think of coated papers as having been associated with the lithographic process only within recent years. Early coated papers were used for the original direct lithographic process, that is, printing from stone plates. Because of the slower press speed, shorter runs, and the nature of direct lithography, the requirements of this process were not severe. With the advent of offset lithography and disappearance of the original process, coated papers were confined entirely to letterpress printing. Offset lithography was widely accepted as a new, much-needed method for printing half tones on the rougher and softer surfaces of economically priced uncoated papers. A characteristic softness of reproduction was obtained in six or more colors and offset became known as a cheaper method of printing. Printing reproduction requiring sharpness of detail and "life" was obtained only by letterpress since the offset half-tone dot was "fuzzy" in comparison to that of letterpress. Furthermore, offset inks on the softer papers lacked the gloss and density of color of letterpress inks.

Developments in offset plate making and inks, beginning in the thirties, improved offset reproduction, particularly the elimination of some of the "flatness" of single-color work. Also, six or more color work became too costly and lithographers turned to four-color printing used by letterpress. At the same time the public's taste changed to printing and advertising with more snap and brilliance. Lithographers turned to coated papers to help achieve the desired result. Many of their early experiences with coated papers were unsatisfactory because coating was not yet properly developed for offset. Letterpress coated was used in many instances with unfortunate results before it was realized that a satisfactory coated paper had to be designed for offset. Also, the running of coated paper on an offset press differed from that of uncoated and pressmen had to become familiar with the specific printing problems coated paper presented. Unquestionably, coated offset papers have been greatly improved since that time. However, room for improvement still remains and it is necessary for constant interchange of information and ideas between the lithographer and coated paper manufacturer to have development keep pace with progress in the offset field.

## OFFSET AND LETTERPRESS IN CONTRAST

Let us first consider the essential differences between letterpress and offset printing. Letterpress reproduction is a direct transfer of ink from a raised plate surface to paper involving certain physical properties of ink and paper without the direct aid of chemistry. The factors are plate, ink, and paper, the plate or printing surface contacting paper only where the printing image exists. The plate itself is sturdy and chemically stable and has no tack of its own when contacting paper surface. Tack results entirely from ink film on the plate, the thickness of which can be varied considerably by fountain adjustment.

By contrast, offset reproduction is an indirect transfer of ink from plate to blanket to paper involving not only physical properties of paper and ink but chemical principles as well. In addition to ink on the plate, moisture exists on plate and blanket, pH is involved, and the plate itself is not just a mechanical surface but rather a surface phenomenon involving areas that are either water receptive or grease receptive. Chemistry is operating at the plate surface, and the plate is not stable under a variety of conditions as in the case of letterpress. For example, the offset plate is subject to oxidation, damage due to abrasion or to unfavorable chemical conditions such as the presence of alkali which can destroy the line of demarcation between printing and nonprinting areas. Furthermore, there is 100% contact between printing surface and paper except for the small gripper margin irrespective of the degree of ink coverage on paper. Not only does the tack of the ink film exert a pull on paper surface but the tack of the moistened rubber blanket as well. The actual printing surface or rubber blanket changes with age and usage due to oxidation, oil absorption, etc. The offset method transfers a much thinner ink film to paper (approximately two-thirds) than letterpress and also may have a moisture content as high as 15%. Consequently, lithographic inks must be more concentrated tinctorially than letterpress inks, that is, the pigment-to-vehicle ratio must be higher.

Offset presses are of the rotary type which means that the rate of printing impression is higher than that of the flat-bed type press, commonly used in the letterpress field. These additional factors present in offset and their various interrelationships make the requirements of offset coated papers more involved than in the case of letterpress. Let us now consider the specific requirements of coated offset papers.

## DIMENSIONAL STABILITY

Offset requires stability of paper dimensions for high quality multicolor printing on coated paper. Dimensional change with respect to paper can result from two causes: (1) change of dimensions due to change in moisture content of body stock, and (2) changes due to mechanical stresses under which paper is placed during printing.

From the lithographer's viewpoint, coated paper should have greater dimensional stability than uncoated paper, the reason being that any lack of such stability causes misregister that is more evident on coated than on uncoated papers and defeats the purpose of using coated paper, namely, to obtain greater sharpess of reproduction and brilliance in multicolor printing.

Wavy edges are an indicator of possible trouble to be encountered in printing as well as indicative of moisture absorption by the paper. The general opinion seems to be that offset coated papers as received are on the dry side and that the average moisture content should be higher, particularly so, where paper is used in air-conditioned printing plants. Wavy edges of paper before arrival are too prevalent. Hanging or conditioning of stock may be necessary to eliminate the wave, and even conditioning will not always eliminate the wavy condition entirely. A wavy stock cannot always be run successfully even on a two or four-color press because the wave undergoes a flattening treatment with each successive color impression that can develop an objectionable "slur" in printing as well as causing misregister between successive color units. The lithographer can print paper with less difficulty if the latter is on the higher side of moisture equilibrium. Then too, coated paper is more difficult to handle and hang for conditioning treatment than uncoated. The coating itself can be cracked in handling, for example, and loosened particles will transfer to blanket during printing. Higher moisture content should help eliminate or reduce curl that develops as a

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result of moisture pickup during printing. Also, troublesome are "puckers" in the sheet which cause misregister as well as "slurs" or "double images" on multicolor presses.

The offset method requires a flat sheet of paper at all times, irrespective of whether paper is printed on a single or multicolor press. Curl, puckers, and absence of flatness can also cause wrinkling to develop at the back edge of the press sheet because as mentioned previously there is 100% contact between paper and blanket and "an open form" which can prevent wrinkling, as in the case of letterpress, does not exist.

Curling and wavy edges at the gripper can cause difficulty in feeding. A satisfactory offset enamel must remain flat whether it is printed in one or more colors on one or both sides. Considering C1S which is a decidedly duplex paper, the coated side must withstand repeated moisture application without the development of curl.

Deformation of paper due to printing stresses is not troublesome if it is within elastic limits and if paper recovers its exact original dimension after impression Any permanent stretch or deformation from applied stresses will affect good printing register unfavorably. Such deformation is more common among the lighter basis weight papers.

## RESISTANCE TO BODY STOCK PEEL OR TEAR

Coated surfaces and rubber blanket come into more intimate contact than in the case of uncoated papers. This more intimate contact in the presence of moisture and ink imposes greater pulling stresses on the paper as it releases from the blanket immediately after impression. Not only must the coating resist lifting from body stock but the body stock itself must have sufficient "cohesive" or bonding strength to prevent peeling or delamination of itself. If it becomes necessary to thin or soften the ink to avoid this, then a muddy appearing and poorer quality print results. If press speed has to be reduced to avoid peeling of body stock, press production is lowered. Generally, lithographers do find it necessary to soften inks and to reduce press speeds when running coated paper both of which adjustments are undesirable. Buyers of offset printing demand more gloss and density of color as well as greater sharpness. This means that coated offset should have stronger body stock to enable the lithographers to use stiffer inks and print heavier solids without the danger of body stock peel and tearing at the grippers Further, the newer, larger presses and forms as well as presses designed to operate at higher speeds require stronger body stock than the older and smaller equipment.

The conventional graded wax test does not satisfactorily measure body stock strength and its resistance to peeling or stripping. A *control* testing method more closely simulating actual press conditions is needed. There seems to be no logical reason to manufacture a coating with greater pick resistance if the body stock itself cannot meet printing requirements since this is analogous to the statement "A chain is no stronger than its weakest link." A precision control test correlating with the stresses to which coated paper is subjected as it releases from an inked rubber blanket and which would evaluate the combined resistance to coating lift and body stock peeling or *surface* bonding strength is needed more today than ever before.

## PICKING OR COATING LIFT

The tack of rubber blanket and ink film as well as the presence of moisture dictate that offset coated must have greater resistance to coating lift than letterpress coated. Heavier forms with greater ink coverage represent more severe conditions in this respect. No only must the coating be sufficiently sized to avoid "lift" but also the entire surface must be free from scale and localized weak spots, such as those due to dirt, resinous or brittle particles that lift from the body stock or coating. The latter particularly can lift from the paper in nonprinting areas as well as printing areas and once attached to plate or blanket can be removed only by press stoppage and wash-ups. The pressman's only means of attempting to eliminate coating lifts is softening of inks which, of course, detracts from the quality of the job as mentioned above.

Process color inks correctly formulated for multicolor presses must be graduated tack-wise to trap properly. Reducing tack of such inks by the pressman to overcome picking interferes with proper trapping of wet colors, in addition to sacrifice of color density and the possibility of a greasy condition developing on the plate.

## CHARACTERISTICS OF COATED SURFACE

The greater approach of a coated surface to optical flatness as well as its highly reflective power enhances the appearance of offset inks and half tones. For maximum brilliance in the print, a very level, dense coated surface is needed. However, such a surface is more likely to cause offsetting in the delivery pile because of denser packing. Further, other requirements must be satisfied. Any greater tendency of a highly finished, coated surface to cling to the blanket thereby necessitating reduced press speed and softer inks is again defeating efforts to achieve maximum brilliance of printing. Therefore, the nature of the coating should be such as to minimize its adherence to blanket after impression. Coating pigments, degree of ink absorbancy, and surface contour determine the ease with which coating and blanket separate. Obviously, the lesser degree to which coating "sticks" to an inked rubber blanket, the greater will be the effective resistance of the paper to peeling or tearing. Further, excessive forces required to pull the paper from the blanket in the case of large areas with complete ink coverage can cause a mechanical breaking or alteration of the paper structure resulting in curl, reverse embossing, or tail-end-hook. The most desired coated surface for general lithographic purposes is that having a flatness and density of surface consistent with satisfactory press performance and production.

## INK RECEPTIVITY

From the standpoint of press performance coated paper should be highly receptive to ink vehicle in order to minimize or eliminate offsetting at the delivery pile, to reduce or eliminate the use of antioffset treatment, and to make it possible to run full-size loads with any press form. Half-tone dots are reproduced with greater sharpness and ink films lay with less mottle and dry with greater density of color on a coating more receptive to ink. A coating which promotes a rapid, initial setting of a freshly printed ink film is desirable particularly so in the case of wet-color printing where successive ink films are superimposed in an interval of several seconds. Rapid absorbancy of ink vehicle gives better trapping with cleaner and sharper dots.

Conventional laboratory methods of measuring ink absorbancy are not sufficiently sensitive to determine the rate at which a freshly printed ink film sets on a coated surface.

## CHEMICAL CONSIDERATIONS

The lithographic principle is based upon the fact "that grease and water do not mix." However, this is not strictly true in practice. Earlier it was said the moisture content of the ink can be as high as 15%. Generally it will average between 25 and 15% and is present as a water-in-ink emulsion. One of the reasons for maintaining an acidic condition during press operation is to help stabilize this emulsion. A neutralization of press acid or raising of pH such as that resulting from action of coating alkalinity will invert this emulsion or cause an ink-in-water emulsion to develop and, as a consequence, an over-all tint to form on the plate and print on the paper. The acidic condition is necessary not only to avoid the occurrence of the above but also to maintain sharpness of image and to preserve the plate. The actual leaching

of alkaline components from the coated surface by press moisture and transfer of such from paper to plate thereby unbalancing chemical conditions on the press will result in difficulty. The earlier use of alkaline coatings was unsatisfactory in many instances no doubt due to the fact that such coatings did not possess the necessary water resistance to prevent the transportation of alkalinity and active metallic salts from paper to plate via press moisture.

Although an acid pH is essential for satisfactory press operation, it has been known for some time that acidic conditions and low pH retard the drying of lithographic inks whereas alkaline pH increases the drying rate. This effect becomes more pronounced as the moisture content of the ink film is raised. It is the amount of moisture in the paper at the delivery pile that affects the drying of ink and the amount of such moisture present as the ink dries depends upon these factors: (1) amount of moisture originally present in paper before printing, (2) amount of moisture added by pickup during printing, and (3) the relative humidity surrounding the paper which in turn affects moisture gain of or dissipation from the printed pile. With reference to factor (2) added press moisture is subject to a greater degree of entrapment in a pile of coated paper than in the identical size pile of uncoated paper due to the more compact mass of the former.

This leads us to consider the fact that acidic conditions are necessary in the ink film until it has been transferred to paper, but once it is on a paper surface, an alkaline coating is highly desirable so as to facilitate drying. In addition, an alkaline pigment, such as calcium carbonate, has excellent ink receptivity and its presence, to a certain extent, is therefore beneficial. Consequently, the coating should have the necessary moisture resistance to prevent chemical activity between itself and the offset plate and inks.

Further advantages resulting from greater moisture resistance of coating and the consequent use of less water in the lithographic operation are stronger, denser inks, less likelihood of moisture curl, and changes of dimension due to moisture expansion.

## CLEANLINESS OF SURFACE

A high quality coated offset paper lacking cleanliness of surface is like a fine automobile with engine trouble. Neither will give satisfactory performance. The presence of any extraneous dirt spells trouble to the pressman. The offset blanket is a highly efficient dirt catcher and removes any superficial dust, lint, or dirt particles from the coated surface in both printing and nonprinting areas, all to the sorrow of the pressman. Generally speaking, offset coated could require less frequency of wash-up, the necessity for frequent wash-ups now being: (1) too much surface dirt prevalent, (2) higher quality work on coated paper requires cleaner plate and blanket, and (3) the more intimate contact between coated surface and blanket leaves less available space or clearance where small particles can exist without critically affecting quality of reproduction.

Earlier it was mentioned that an offset plate does not have the chemical stability of letterpress plates. Each time an offset press is stopped for plate wash-up, the life of the plate is shortened due to oxidation and the use of etching solution for thorough cleansing of plate. Consequently, a paper necessitating frequent press wash-ups in an endeavor to produce a presentable job of printing not only lowers production but lowers plate life. Dust or dirt in coated offset can be present in two ways: (1) Present as a fine dust or particles existing over the entire paper surface which gradually accumulate on blanket and plate and interfere with sharp dot reproduction. Such dust appears as it might have originated from flying particles during slitting that either became imbedded in the surface or were statically attracted thereto. (2) Second, the presence of large particles, with or without fiber, often found in greater concentration at the edges of the sheet. These appear very definitely as a white deposit on the blanket and often in the form of streaks coincident with the sheet edge. In either case any such dirt particles are a "headache" to the lithographer and from his standpoint there could be a general improvement.

## MISCELLANEOUS REQUIREMENTS

Opacity is a characteristic of paper to be considered for most printing requirements. Although many offset printing forms consist of large, heavily inked areas, coated papers generally have satisfactory opacity. With respect to opacity, the requirements of offset are less severe than letterpress because the printed impression from the offset blanket has less showthrough than the impression from the raised surfaces of letterpress.

It is very important that coated offset be trimmed square and not just simply trimmed four sides. Further, the edges, the gripper edge particularly, should form a perfectly straight line and should not be bowed. When bowed edges or off-square sheets are encountered the lithographer usually finds it necessary to retrim paper before printing.

Offset papers require long grain to minimize dimensional change and to give best press register. Grain direction and longer sheet dimension will be parallel to the cylinder axes; therefore, a lower percentage of dimensional change will occur in the across-the-cylinder direction. This is desirable because no compensation for any dimensional change can be made in this direction once a set of color plates has been made. Likewise, the greater percentage of dimensional change across the grain or in the direction of shorter sheet dimension occurs in the around-the-cylinder direction, and for multicolor work, compensation for any change in this direction can be made to some extent by adjusting the packing of plate and blanket cylinders. In the event paper has wavy edges, the greater degree of waviness develops across the grain. When grain is long, this greater degree of waviness extends in the around-the-cylinder direction and has more of a chance of being worked out of the sheet without forming wrinkles by the "ironing" effect of the offset impression. Waviness in the cross-cylinder direction is more likely to cause trouble and form sheet wrinkles and therefore should always be minimized.

## CONCLUSION

Coated papers require better handling in every respect by the lithographer, or briefly, coated is more critical than uncoated during lithographic operations. It is obvious, therefore, the highest possible uniformity exists within a given delivery of paper as well as among different deliveries. Uniformity of quality means that press conditions, inks, etc., can be standardized to a greater extent thereby assuring higher production and better results in printing.

Offset lithography has become a precision method of high quality single and multicolor reproduction in which coated paper seems destined to play an increasingly more important part. A greater volume of offset printing will be on the economically priced on-machine-coated papers following the similar development that has taken place in the field of letterpress printing. At the same time lighter weight coated will be used to a great extent, the minimum weight being determined by the physical limitations of manufacturing coated paper for satisfactory offset performance. Substance 60 pounds will be demanded to a greater extent for sheet-fed printing, and substance weights below 60 pounds will be used in substantial volume for web-fed offset in the field of publication and specialized printing as soon as they can be satisfactorily developed.

The requirements of coated offset are relatively severe but it is felt that they will be challenged and satisfactorily fulfilled by the paper industry as offset lithography continues its remarkable growth in the graphic arts industry.

Presented at the Second Coating Conference sponsored by the Technical Association of the Pulp and Paper Industry, Boston, Mass., April 18–20, 1951.

# Safety Papers—A Review of Theory and Practice

FRANCIS L. SIMONS

The term "safety paper" has been in use in this country since 1845 and in England since somewhat earlier. Its meaning, however, is still rather vague to most people and very frequently it is loosely used to describe almost any kind of fraud-preventive paper. As is pointed out later in this discussion, the phrase "safety paper" can best be used in a more restricted sense in order to distinguish these products from banknote and currency papers.

Although this review is intended to cover safety papers only, it is recognized that a discussion of banknote and currency papers must be included in order to give a rounded and complete picture. However, this inclusion is limited to essential illustrations of basic theory.

It has been the author's observation over a period of many years that even technical people have some grave misconceptions as to basic theory and general principles of document protection. This may well be due to the very limited literature on the subject. There is also a similar confusion of thought in regard to the manufacture and use of fraud-preventive devices, particularly in the case of safety papers. It is not generally realized, for instance, that the major tonnage of our safety papers is in the 100% wood pulp grades, nor that the annual production in this country passed the 10,000-ton mark years ago. Neither is it generally understood that most of our safety papers are not produced as such in a paper mill but are made by converting or printing operations with plain white paper as the starting point. As banknote papers do commonly have protective features built into them at the paper mill it is frequently and erroneously assumed that all safety papers are made likewise.

Under these circumstances, something more than a simple patent digest appears to be both justified and needed. Accordingly, Part 1 following constitutes an outline of the basic principles of document protection, Part 2 is a discussion of selected patents illustrating these principles, and Part 3 is a classified patent bibliography. An attempt has also been made to word the discussion so that it will be at least broadly understandable to the nontechnical reader.

## PART 1—GENERAL PRINCIPLES

To start at the very beginning, we should observe that our whole financial system depends on documents and their exchange. The temptation to fraud is widespread, therefore, and it is necessary in many cases to protect documents against forgery or alteration not only by penalty of law but by mechanical and chemical devices.

In developing and using these protective devices it must be recognized that all documents are exposed, in greater or lesser degree, to two distinct and separate manipulative risks (*1*). These risks are:

1. The risk of being counterfeited or imitated or duplicated *in toto*. By this we mean the complete manufacture "from the ground up" of counterfeit currency, bogus ration stamps, spurious pay-roll checks, etc. Successful counterfeiting usually results in the issue of large numbers of spurious documents, and might be called a "mass-production" fraud when compared with No. 2 below.

2. The risk of being altered or changed to a different value or intent. By this we mean the fraudulent alteration of what was originally a genuine document, such as the "raising" of a check, or the changing of words or figures on receipts, tickets, contracts, etc. Contrary to No. 1 above, a successful alteration results in the issue of only one spurious document for each manipulation.

These are quite different risks and should be separately appraised for any given case, always remembering that the crook is just as alert to values as anyone else and will attack where there is the greatest return for the least effort. It may be logically suspected that counterfeiting is the field that attracts the skilled professional forger, and that it is the "amateur" crook who tries his hand at an alteration occasionally.

### *Protection Against Counterfeiting*

To guard against the first risk (counterfeiting or complete imitation) we use watermarks, silk fibers in the paper, ornate and complex engraving, etc. Such devices may best be referred to as "authentification devices" or "marks of origin"; to be of value they must be produced by methods not available to the criminal, and it must not be possible to imitate them by other and simpler processes. The true watermark is one of the oldest of the authentification devices and is still one of the most satisfactory.

It should be remembered that, in principle, these marks of origin are used to supplement a signature. In general, all documents are validated by signatures even though in many cases the latter are printed and not hand-written. The supplementary authentification device requires the crook to counterfeit or forge something more than just the signature and in banknotes, for instance, these devices (such as complex engraving) far outweigh the signature in importance and effectiveness. However, in the case of simple documents of low value or documents whose counterfeits are difficult for the crook to sell, an authentification device beyond a plain signature or simple printed form is frequently unnecessary.

The tests of a good authentification device or mark of origin might be listed somewhat as follows: (1) It must be produced by methods (a) that require large, expensive, or otherwise inaccessible equipment; or (b) that are complex, difficult, or require a very special skill or rare materials; or (c) that are completely secret except to a very few people, and that are impossible for the forger to detect by test. If the method in question complies with more than one of the above tests, so much the better. (2) Each mark or device must be properly identified with the validating signature, unless it is the validating element of itself, and paper carrying it must be guarded against theft at all stages of manufacture and use. (3) It must be impossible to duplicate or imitate, or even to make an approximate imitation by other and simpler methods such as would be readily available to the forger.

### *Protection Against Alteration*

In guarding against the second risk to which documents are exposed, fraudulent alteration, we must first note that an alteration includes two steps. Original printed or written matter must first be removed by some form of erasure, and then new matter must be written or printed in its place, assuming of course that the document is properly laid out so that a simple addition of new matter is not possible (*2*). Therefore, our efforts are directed to making erasure difficult or impossible, or to the use of forms and styles of writing or printing that the criminal finds it hard to match or duplicate when he attempts to insert new material.

To prevent erasure we can use indelible inks, mechanical check-writers which perforate or shred the paper, chemicals in the paper which "fix" ink or printing so that they cannot be removed, or soft and absorbent paper which does the same thing. We can also use chemicals which develop colors or stains when chemical erasure is attempted or we can use a fugitive or nonfast dye which is easily destroyed by chemical ink eradicators. If the document is of the fixed valuation type (e.g., bonds or banknotes) we also depend on its layout, repeating the essential figure or statement of value many times so that the crook must make many separate alterations just to change one document.

FRANCIS L. SIMONS, Member TAPPI; Crane & Co., Dalton, Mass.

Tests of the value of a given antialteration device are not easy to formulate and are largely a matter of skill developed by the user or maker of protective papers. In the first place documents may be printed, typed, or handwritten and the methods of erasure for these different kinds of inscription are different. Again, such tests can hardly be standardized to include the personal skill of the forger. However, tests can be devised that are very useful in making comparisons and in enabling the safety paper user to reject commercial offerings that are seriously inadequate, or that are overpriced for the degree of protection afforded. The main point to remember is that the safety paper must show some kind of reaction with any agent that will remove the written or printed parts of the document that determine its value.

First in such a group of tests is mechanical erasure, using both hard and soft rubber erasers as well as a draftsman's or engraver's knife. If the safety paper is effectively protected, the inscription cannot be removed without visibly and unmistakably damaging the surface of the paper or else a color, tint, or background pattern will also be removed, and its absence will be apparent. Such an erasure test should be made on an actual inscription and should be carefully done as the crook would naturally do it, that is, the area of erasure is kept as tiny as possible, covering only the actual lines or letters to be removed. Obviously the test inscription should not be of a type that would be firmly attached to *any* kind of paper, and therefore very difficult to erase anyway, as in this case the permanency of the inscription is the determining factor rather than the quality of the safety paper.

The testing of an antialteration device for its protective value against chemical erasure is somewhat more complicated, but nevertheless it can be set up to give useful comparisons. As in the case of mechanical erasure tests, chemical eradicators are applied only to the actual lines of the figures or letters to be removed, using a stainless steel pen or other fine-pointed tool. Even the amateur crooks know better than to swab a chemical solution over a whole word or the whole body of the writing, yet many users and makers of safety paper do their testing or demonstrating in just this way. Osborn (*2*), dean of American experts on detection of forgeries, called attention to this fallacy years ago.

The possible number of eradicator chemicals is large but acids, alkalies, oxalates, bisulphites, hypochlorites, permanganate, hydrosulphite, and their combinations will serve as representative types. The common bookkeeper's chemical ink eradicator usually includes a bottle of oxalic acid and one of sodium (or calcium) hypochlorite, although a so-called one-bottle type is available in which the hypochlorite is mixed with a salt of oxalic acid. In Europe an ink eradicator kit consisting of dilute acidified permanganate and sodium bisulphite solutions is quite common as it possesses an advantage in leaving many papers in better condition to write upon after an eradication. Hypochlorites and other alkaline chemicals used as ink eradicators generally destroy the sizing so that it is difficult to write again over the treated spot. However, this is a natural property of paper in general and an incidental rather than a planned feature of most safety papers. Any eradicator being used for test should be first diluted to the point where it is barely effective in removing a test legend.

If the protective element is a surface color or design, both mechanical and chemical erasure tests should be followed by an attempt to restore the obliterated portions of the color or design. This is a step almost universally forgotten or ignored, yet it is obvious that the mere destructibility of a surface pattern by erasure is no protection if the pattern can be readily restored. As most of the safety papers in common use today are printed or lithographed with such a design, this is an important point to check. The main reason for using a pattern instead of a flat solid color is the added difficulty of making such a restoration, as is pointed out in U. S. pat. 123,782 (LaMonte and Saxe) and by Meyer (*1*) (p. 126). These patterns are therefore functional as well as ornamental.

***Concealed Protection***

Protective devices of all kinds, both authentification and antialteration methods, may also be divided into two broad classes: (1) those devices which are visible to and are recognized by everyone (such as a watermark), and (2) concealed devices (such as a fluorescent imprint or colorless chemicals which may be identified) of which the general public knows nothing. There has been considerable argument as to the relative merit of these two approaches to the problem. One school of thought holds that the man in the street should be able to detect a forgery or alteration and thereby stop the crook's activities at the source. The other school feels that with concealed devices the criminal will not realize his work is imperfect, and therefore a forgery is quickly and easily recognized *by those in the secret.* Unfortunately, in our present complex business world, some time may pass before a forged document has moved through various channels of exchange and can be examined by *those persons in the secret,* and meanwhile several innocent intermediaries in the exchange may suffer loss. On the other hand, if the concealed device is made known to enough people so that a forgery can be detected promptly, then the information will almost certainly leak out to the criminal world and the value of concealment is lost. Too much dependence on secrecy can also be extremely dangerous if the concealed device is simple and easily counterfeited, as once it is discovered by the criminal, he can issue counterfeits almost at will. It should also be remembered that in this day of widespread technical knowledge it is very difficult to maintain secrecy of this kind. Nevertheless, the hidden protective device is a powerful weapon in special cases and for special purposes, particularly in the case of documents whose circulation or exchange is closely limited, and if the hidden device complies with the previously given tests for efficacy of visible devices.

The element of secrecy or concealment may have an entirely different aspect in certain cases, however, particularly where the risk of counterfeiting is very serious. In many instances it is necessary to have two sets of authentification devices, one, such as printing or engraving that the public can recognize, and another that is either very complicated or highly technical for the use of the expert.

Secrecy in this case is or should be a by-product simply because there is no use explaining to the public something incomprehensible to anyone but a qualified technician. However, marks of origin of this type should still be just as hard to counterfeit as any other.

This brings us to a final point in this discussion of generalities and that is the fact that in many cases our protection against fraud resides to a considerable extent in the way we handle and exchange documents. Over a long period of years it has grown to be a matter of habit to demand satisfactory identification of the endorser, bearer, or negotiator of a document wherever possible and to require assurances that he will be available for redress if anything is wrong with the document. Washington authorities have emphasized the point, in connection with Government checks, by advertising the slogan "Know your endorser."

This precaution is probably an outgrowth of the Negotiable Instrument Laws and of various court decisions based on them. As applied to bank checks, the trend of the decisions is to the effect that a bank is not only liable for making payment on a forgery of a depositor's signature but is also liable if the endorsement is forged or if the check has been fraudulently altered, providing there is no gross negligence on the part of the maker of the check (*3*). It should be remembered in this connection that while the protective devices that are in or on a general-purpose safety paper can prevent fraudulent alteration, they cannot prevent the counterfeiting or forging of an endorsement signature. To put it another way, the genuineness of an endorsement on the ordinary bank check cannot be determined by reference to characteristics of the safety paper.

Under these circumstances the only way a bank can protect itself is to require identification of an endorser as mentioned above. This is even more understandable when we note that, in general, a bank cannot compel its depositors to use safety paper, or mechanical check writers, or even ink, as in some sections of the country pencil-written checks are common.

Banks and other institutions having adopted this system of demanding identification, it has now become more or less a general principle to be applied to all documents wherever possible, its effectiveness varying with the degree to which it can be applied. In the case of currency and similar "bearer" documents this type of safeguard is inapplicable, of course, but that it is effective in other cases is indicated by the continued substantial use of plain unprotected paper for many checks and other documents of value.

## PART 2—PATENT SURVEY

The term "safety paper" is and apparently always has been rather loosely used to describe any variety of paper that embodies any antifraud feature. The phrase was probably brought to the United States from England by Varnham in 1845 when he took out U. S. pat. 4143 (corresponding to British pat. 10,507 (1845)) for a product he called "Safety and Protective Paper." That the term was well established in that period is further indicated by fifteen British patents for safety papers dated between 1817 and 1856 (*16*). Likewise the term "safety cheque" was in use in England by 1875 and probably earlier (see British pat. 3770 (1875)).

However, a broad distinction is usually made between safety paper and banknote paper. The former shows sensitive chemical reactions, its colors necessarily fade or bleed readily, it is made from almost any fiber, and it is not usually designed for rough service or long life, while the latter has just the opposite qualities and is usually made from cotton, linen, or other strong fibers. Again, all but a few per cent of the safety papers used in this country are made by a converting operation, i.e., plain white paper is coated or printed with erasure-sensitive aniline dyes, and/or in a few cases with reactive chemicals. Banknote papers, however, are usually made with protective features as an integral part of the sheet, produced, like a watermark, as a step in the papermaking process. Rossman (*4*) makes the same distinction indirectly and compares safety paper to chemical test papers.

Perhaps the best distinction is based on end use, as, in general, banknote papers are used for bearer documents of fixed value or denomination while safety papers are mostly used for documents whose value is filled in by the user for widely varying amounts and for a specific payee. There are exceptions, of course, but the generalization explains why, in banknote papers, the emphasis is placed on authentification, while in safety papers it is on preventing alteration.

In presenting the following patent survey, an attempt has been made to classify the items into two broad groups, those pertaining to authentification methods and those involving methods of preventing alteration. There is a great deal of overlapping, of course, as many patents contain proposals for both types of protection, as well as for methods that apply mainly to banknote papers. In addition, the appended list of patents includes three other groups: check protectors, revenue stamps, miscellaneous (equipment and items related to safety paper). It is the writer's hope that this form of survey with appended lists will be just as useful as a much more lengthy item-by-item digest.

Attention should be called to the book by J. B. Meyer (*1*), written in German and published in Switzerland in 1935, as being one of the best sources of information available. The bibliography of 128 U. S. patents published by Rossman (*4*) in 1928 also deserves special mention.

### *Authentification Methods*

*Watermarks.* One of the earliest and still one of the most satisfactory authentification devices is the ordinary watermark. For best results, of course, it should be fairly complex, shaded, or perhaps localized as in many foreign currencies. Colored watermarks have been proposed, but they offer little additional value and have not been used to any extent. "Synthetic" or printed imitation watermarks have also been suggested (Meyer, U. S. 866,293; Smith, U. S. 2,067,988; Sangster, U. S. 228,221; Ruth, Austrian 77,088) and in fact there have been sporadic attempts to market special transparentizing inks for this purpose. Such watermarks are easily counterfeited, of course (see also Boyer, U. S. 2,021,-141).

Ordinary embossing has been used to a very limited extent as a substitute for a watermark, not only for authentification but to prevent alteration (Paquet, U. S. 114,963; Ilch, U. S. 852,840). By first dampening the paper, an embossing press or its equivalent will produce semitransparent impressions, but in general, embossing is too easily counterfeited to be of real value as a mark of origin (see also Oldofredi, U. S. 2,370,-186).

*Laminated Papers.* Next to the watermark, one of the oldest authentification devices is the laminated structure (see Congreve, British 4419 (1819) ). Varnham, in U. S. 4143, proposes such a sheet, the center ply being colored with an easily bleached dye and the two outer plies (liners) left white. This construction also protects against alteration, of course. Olier (U. S. 38,835) presents a modification of the same idea. Present-day pari-mutuel tickets are similarly made, although the colors may be fast and there is usually more than one colored filler. Theoretically such a sheet can be counterfeited by pasting, but this risk is minimized by changing the color combinations frequently.

There are many variations in this lamination idea. For instance in U. S. 2,079,845 (Colbert et al.) and U. S. 2,143,-682 (Brown) a safety carton board is made by printing a legend on the top filler web just before the liner is couched on. If water-soluble inks are used the legend diffuses through the liner and gives the board an excellent mark of identification (see also Brit'ish 4419 (1819) ).

There are many older patents which call for the insertion of various identifying materials between the plies of a laminated sheet. Howell, for example, in U. S. 28,370, specifies a center ply of fabric or of paper carrying designs in metal foil. Carbon paper, perforated bands of tissue, and rubber threads have also been suggested (Brooks, U. S. 210,089; Gernaert, U. S. 964,014; Crane, U. S. 61,321) as inserts in a laminated construction.

The present-day use of such methods is limited to cylinder machine boards for pari-mutuel and other tickets, and for protective (counterfeit-proof) cartons.

*Additions to Furnish.* Authentification devices based on the addition of some special identifying material to the papermaking furnish have been the subject of a large number of patents. Willcox (U. S. 56,650) and Hayward (U. S. 34,-634 and 225,279) propose silk and other fibers (*5*), and Schaffner (U. S. 59,281) suggest metal powders. United States currency has long been identified by colored fibers.

Chamberlain suggests metal-plated threads (U. S. 2,143,-406), Whitehead (U. S. 2,208,652) proposes synthetic fibers, and Sanburn (U. S. 1,938,543) suggests fibers treated with distinctive chemicals responsive to test. The treated fiber idea is old, with many variations, most of them of little value.

Macdonough (U. S. 447,336 and German 61,460) discloses the usefulness of planchets—tiny pieces of colored tissuelike confetti—as an addition to the furnish. Printed planchets are suggested by Fues (German 422,294). Planchets have been in common use in banknote and money order paper for many years now; they may be of various materials, colors, and geometrical shapes and they may be scattered or localized so that many combinations can be worked out for identification purposes (see also Schlitz, U. S. 1,929,828).

In this country planchets, silk fibers, etc., are used mainly in banknote and money order papers.

*Test Chemicals.* Another group of authentification devices includes special chemicals which will show a color reaction when tested by the proper reagent. Such chemicals may be added in the beater, used as a surface coat, or printed on the sheet as an invisible design (*6*). Jameson (U. S. 137,-775), Bayle (U. S. 1,899,452), Sanburn (U. S. 1,929,543), Lum (U. S. 1,990,994), Grafe (German 397,363), and Lebateux (Austrian 10,301 and 12,999) give typical examples. Our wartime gasoline ration coupons were authenticated in part by this general method.

Such methods belong to the class of concealed devices to which reference has already been made. Once discovered they are easily counterfeited unless the chemicals are so chosen that they give a very peculiar series of test responses, or a response only with one or two special reagents whose nature and source are well-guarded secrets.

A variation in the test chemical idea is the printed legend covered by a clay-casein coating as suggested by Himmell (U. S. 1,998,237; see also 1,825,796). When the coating is moistened with water it becomes transparent and the legend is visible, thus serving as a mark or origin. When the coating dries out again, the legend disappears and the test can be repeated at will. Simons and Weiss (U. S. 2,129,362; -3; -4) have suggested similar methods.

*Fluorescence Methods.* Invisible imprinting or over-all impregnation with fluorescent chemicals has been and still is used in various tickets and coupons (*7*). Fluorescence has also been used as a mark of authentification by appropriately treating a small percentage of the fibers in a sheet as in the making of "granite" papers. Under an ultraviolet lamp such fibers stand out plainly, providing there is not too much overprinting on the document. This method was used in some war ration coupons both here and in England.

The most important patents in the fluorescence group are those of Huntress (U. S. 1,822,098 and 1,822,148) which claim the basic idea of using fluorescence for identification. Block (U. S. 1,771,612) also discloses the same idea but claims only the use of aesculin as the fluorescent chemical. Other patents disclosing fluorescent materials or methods include Paine and Radley (U. S. 2,089,293), Clifford (U. S. 2,255,696) and I. G. Farben. A.-G. (German 497,037). Fluorescence methods are very spectacular and to the layman they appear more effective than is usually the case. They are open to all the objections to the class of concealed devices, and in the case of simple imprints or designs are easily counterfeited.

There have been various other proposals for authentification devices, such as coloring on the paper machine in strips or bands (Syms, U. S. 177,896), the use of x-ray-sensitive materials (Stirm, German 337,818), and the use of iron particles which may be magnetically detected (Reinheimer, German 416,302; -3). Even radioactivity has been suggested. However, the classes already described include those which have had any commercial success in this country.

*Printing and Engraving.* Before leaving the subject of authentification methods, it should be noted that printing of one kind or another is most commonly used as the principal mark of identification for documents in general. High quality steel engraving as in banknotes and bonds, and skilful lithography as in many bank checks are used a great deal for this purpose, either with or without a watermark or other mark of origin in the base paper. However, this general subject of authentification by printing methods applies most directly to the banknote type of document and is not included in the present discussion.

### *Protection Against Alteration*

*Document Layout or Design.* Of principal interest to us here are the various proposals, such as for a colored silk thread, to designate and limit the value of a banknote. Most authentification devices may be used in this way to prevent alteration, but the method is applicable only to documents of fixed value or denomination and cannot be conveniently used in the case of bank checks that are written for widely varying amounts. An exception is the U. S. Postal Money Order where alteration of value beyond a narrow range is prevented by tearing off limiting-value tabs on one end of the form.

In the case of fixed-value documents their layout can be of great importance. If the amount is repeated many times in the engraving or printing, and in forms, styles, and colors quite different from other denominations of the same document, an alteration then becomes too lengthy a task to be profitable.

Patents in this connection include U. S. 84,341; 193,221; 202,515; 225,279; 894,664; 1,597,607; German 341,970. The photographing of bank checks for record purposes is of interest here also (German 464,344; 492,546).

*Ink-fixing.* If paper is either made or afterward impregnated with chemicals which will react with writing ink (or one of its ingredients) to produce very insoluble and permanent compounds, we may say that the ink is "fixed." When properly carried out this can make either mechanical or chemical erasure difficult or impossible, and thus prevent fraudulent alteration.

One of the earliest patents (British 4131 (1817)) proposes steeping paper in a soluble ferrocyanide as a means of accomplishing this sort of "ink-fixing," as ferrocyanides react with the iron in an iron-gallotannate ink to form Prussian blue in and on the fibers of the paper. Prussian blue is an insoluble pigment which resists chemical attack except by methods which usually disfigure the paper.

In the last century, when checks were almost all handwritten, the method was of value. Nowadays, when so many checks and most other documents are typewritten, the usefulness of the method is rather limited. For present-day conditions a safety paper depending on this concept should include means for "fixing" not only iron-base writing inks but also aniline inks and typing. The nearest approach to this is a soft, absorbent paper structure or an absorbent pigment coating that tends to "fix" any kind of impression mechanically. As a matter of fact, it has been pointed out repeatedly (*1, 2, 8–11*) that a hard, strong, well-sized paper actually assists the forger in making alterations as he can use drastic methods without destroying the paper itself. If, on the other hand, the sheet is soft, slack-sized, of low strength, and contains a filler (an uncoated book paper for instance) an alteration is difficult even without special preventive devices, particularly if the document is typed. In prewar Europe, this type of sheet was quite freely used as a safety paper base, but in this country competition has placed too much emphasis on sheet strength to allow such a paper to be commercially successful. Most safety paper users have gotten into the habit of demanding a product with the strength, snap, and appearance of high-grade writing papers, even though these factors seriously diminish and may even nullify the value of any protective features.

Ferrocyanides, both soluble and insoluble, are suggested as ink-fixing reagents in a long list of patents. Most important are Loewenberg (U. S. 53,081), Schreiber (U. S. 322,131), Hill (U. S. 330,894), Schlumberger (U. S. 443,116), Hoskins and Weis (U. S. 511,271), Schmidt (U. S. 1,217,076), Wood (U. S. 1,900,967), Simons (U. S. 2,037,937), Gethe (German 328,787), and Mache (French 269,012).

Thiocyanates are proposed for the same purpose by Barclay British 1390 (1859)), Herapath (British 1628 (1858)), and (Benzies (British, Prov. 2075 (1911)), tannin and tannic acid by Foster and Wyman (U. S. 227,559), Ford (U. S. 243,342), and Clapp (U. S. 305,292), and phenanthroline by Simons (U. S. 2,186,810). Of these various suggested chemicals only the insoluble ferrocyanides are used commercially today. There

have been sporadic attempts to use soluble ferrocyanides as they can be applied more cheaply in an impregnating operation, but unfortunately the soluble compounds are unstable and discolor on aging, or else the stabilizing chemicals added, such as alkalies or phosphates, introduce other problems.

*Structure.* Under this heading we should note such patents as that of Snyder (U. S. 1,910,568) which calls for a tissue paper facing and U. S. 1,727,912 which proposes a thin casein coating on an unsized base sheet. The theory here is that an attempted alteration will rupture the tissue or the casein coating and make the inscription of a new legend impossible. Bradt (U. S. 2,333,979) makes a similar suggestion but adds sensitive chemicals to the coating. In the writer's opinion, the principle is sound and worthy of more attention, but the appearance and feel of a laminated or coated sheet apparently have not appealed to most safety paper users, and such a sheet has never had any great commercial success (see also Houssmann, German 303,989 and Steuer, German 497,178). Goodman (Waterlow & Sons) in British 159,740 proposes using a light-colored coating over a dark-colored base paper as the use of eradicators removes the coating and exposes a dark spot.

*Fugitive Tints or Colors.* The simplest and cheapest and therefore the most widely used method of protecting against alteration, particularly of handwritten documents, is the use of colors or tints which will be destroyed or bleached when the forger attempts to make an erasure. We speak of such colors as being "fugitive" or "deleble" and the principle involved is that they shall be as easily bleached or erased as the inscription on the document. Such colors may be applied in the beater, as a surface coating, or by any form of printing.

A great many of the early patents are based on this method, among which we should mention Newton (British 9771 (1843)) Varnham (U. S. 4143), Lea (U. S. 38,231), Olier (U. S. 38,-835), Jones (U. S. 54,834), Gibson (U. S. 41,118) and Kellogg (U. S. 77,887). These earlier workers used Prussian blue, indigo, and other natural colors, but the development of coal-tar dyes about 1870 made a much wider range of colors available. The early aniline colors were, as dyes go, of rather poor quality in that they faded and bleached easily and were not at all "fast," but these are exactly the properties required in a fugitive safety tint. Fading, of course, is not exactly desirable, but if the dye is of the type easily destroyed by chemical ink eradicators it is almost certain to fade readily. The simpler acid and basic dyes were and still are the ones commonly used, although there has been some recent improvement in fading through the use of the so-called "metallized" dyes.

Thomae (U. S. 101,786 (1870)) seems to have been about the first in this country to propose a safety paper based entirely on the use of aniline dyes. He suggested their use directly in the beater, but Willcox (U. S. 115,005 (1871)) observed that the dye could be applied as a surface coating or stain on previously finished paper. LaMonte, Saxe, and Clayton (U. S. 121,946 (1871))simplified this idea somewhat and suggested putting the dye in the tub sizing as this was more economical. These proposals of Thomae, Willcox, LaMonte, et al. refer, of course, to a flat solid color exactly similar to what is today produced by calender staining. However, the earlier English and Continental workers, such as Newton (British 9771 (1843)) were the first to suggest a printed design or pattern in fugitive colors (see also Johnson, British 1386 (1856), Nissen, British 1,228 (1860), Luttich, German 283,752, and Walther, German 402,727). Although some solid-color safety papers are produced nowadays, most of the surface tints are in the form of a pattern.

If we include all types, a large proportion of our surface-colored safety papers is now produced by printing methods, lithography being frequently used, although the aniline press is probably best adapted for such work. For best results, the printing method chosen should apply the fugitive tint in such a way that it does not penetrate and is not mordanted or otherwise attached to the fibers too firmly or bound to the sheet by the printing vehicle (see Simons, U. S. 2,331,575).

However, two nonprinting methods of applying fugitive colored patterns to paper surfaces are worth mentioning in particular, one for its historical interest and the other because of its considerable use today.

One method was suggested by Duthie in 1872 (U. S. 125,-550) who specifies that the fugitive color be applied by ruling, and that the color consist of ordinary writing ink thinned down somewhat. In selecting writing ink for the coloring material Duthie goes to the heart of the matter in that his fugitive color is certainly as sensitive as pen writing.

The other nonprinting method of applying colored patterns is described in U. S. pat. 123,782, also issued in 1872. In this patent (entitled "Improvement in Figure-Tinted Paper") LaMonte and Saxe disclose that when color is added to a paper machine size-tub and one of the two size-tub squeeze rolls is engraved with a pattern, then the paper will carry a reproduction of that pattern in the form of light and dark shades of the color used. The process is explained in more detail in patents to Madden (U. S. 1,666,031), Gailer (U. S. 1,692,645), Bassford (U. S. 2,180,387), and in particular in the patent to Samson (U. S. 2,403,461); the use of the paper machine size-tub as the point of operation has long since been discarded, finished white paper now being made first and then colored in a separate converting operation.

The essential principle involved is the effect of heavy compression or mild crushing on a web of paper, which as all papermakers know, weakens the sizing and increases the absorptiveness for aqueous fluids. As described in the above-mentioned patents, a web of any suitable white paper is passed through a color bath, and then while still flooded with color, between two rolls, one of which is engraved and the other plain. In going through the bath the entire sheet takes up some color on both sides, but under the pressure or impact of the high points in the engraving the color is absorbed more deeply at these points of lowered water resistance. Compression is transmitted through the sheet, of course, so the same extra absorption takes place at these points on the back of the web. As explained by Madden (*loc. cit.*), the greater the pressure the deeper the color. There is thus produced a tinted pattern on both sides of the sheet simultaneously (in reverse or mirror image on the back) in two tones of one color, and of soft or even hazy outline.

As the process partially destroys the sizing of the original white paper and also lowers its physical strength, it is necessary to start out with a base paper of higher strength and harder sizing than is desired in the final product. One or two manufacturers using this process add starch to the dye-bath to offset this loss of sizing but this makes the imprint even more hazy and indistinct.

Papers tinted by this method can sometimes be identified by application of any unusually penetrating writing ink. Such an ink will spread along and tend to strike through the lines of the pattern where the sizing has been weakened. However, the colored design is on the surface only, and does not go through the sheet as is sometimes supposed.

The process is closely related to calender staining and like the latter is continuous, fairly high speed, and economical. Understandably, the product has had a long history of usefulness and has been of major importance in this country.

The scope and adaptability of the process are sharply limited by its very nature, however. Being an absorption process it cannot well be used for fine, sharp detail, especially on the reverse side. It is also limited, practically, to one color (monotones). The reversed appearance of the design on the back of the sheet cannot be avoided either, although this can serve, under optimum conditions, as an authentification device.

*Stain-Producing Chemicals.* The protective value of surface tints, as discussed in the previous section, depends on the forger's inability to restore the color or pattern destroyed during his preliminary erasures. However, it is easily pos-

sible in many cases (*1, 2, 13*) to make such restorations, especially where the color is a flat tint or the pattern is broad and simple instead of fine and sharp, or where the color is very light in shade.

That this risk is generally recognized is demonstrated by the large number of patents issued and by the extensive searches made by most manufacturers of surface-colored safety papers for what we may call "stain-producing" chemicals. Such chemicals are colorless or very light-colored materials which turn dark or develop dark-colored stains when a chemical ink eradicator is applied to paper containing them. The theory is that while a bleached or erased surface tint can be restored, it is impossible to cover up a dark stain (*8*). Curiously enough, the lay public has long had the erroneous impression that all safety papers are full of such chemicals.

Ferrocyanides were among the first stain-producing chemicals proposed, and the fact that they can also be ink-fixing agents, as already mentioned, has made them doubly interesting. In prewar Europe, both lead and manganese ferrocyanides were commonly used; in this country lead ferrocyanide has been employed to a very limited extent. The patents already referred to under ink-fixing also describe the use of ferrocyanides as stain-producing materials, the most important being Barclay (British 1390 (1859)) and Schlumberger (U. S. 443,116). It should be noted that the heavy metal ferrocyanides are insoluble and must be added in the beater (like so much filler) or applied as a coating with a binder.

Among the simpler stain-producing materials are soluble manganese or cobalt salts, and soluble iodides or iodates. These have an economic advantage in that they can be applied as a bath treatment to finished paper. However, manganese compounds produce a stain only with alkalies and hypochlorites, and iodides only with hypochlorites, and furthermore the warning stains developed by any of these compounds can be easily removed by other simple chemicals. Under such circumstances these materials are of little value except in conjunction with other stain-producing chemicals; their occasional use alone is probably in response to misguided and uninformed demand. Patents covering these substances include Menzies (U. S. 302,758), Carvalho (U. S. 531,507), Schmidt (U. S. 1,269,863), and Genoese (U. S. 1,626,078 and 1,804,978).

None of the materials so far named produces a disfiguring dark stain with hypochlorite ink eradicators that is permanent against further chemical treatment, and if such stains can be easily bleached out again, it is a fair question as to whether anything has been gained. However, one class of chemical compounds, the organic amines, does give permanent dark stains with hypochlorites, and therefore affords satisfactory protection *against this one eradicator chemical*. The amines should therefore be used as an adjunct to other stain-producing chemicals.

The simplest of the amines, aniline, has been suggested by Weis (U. S. 1,172,414) and Neff (U. S. 1,578,908) but experience has shown that all of the simpler amines, and most of their salts that are soluble, will discolor badly on aging. By far the most successful amines are benzidine and diphenylamine, whose sulphates are insoluble, practically white, and quite stable. Their value was discovered by Sammet in 1925 (U. S. 1,535,861; -2; -and 3) and since that time a tremendous amount of research has been carried on in an attempt to uncover other amino compounds of equivalent usefulness and lower cost, or to find satisfactory amino compounds that are soluble and can be applied to paper in an impregnating bath. The compounds proposed include sulphanilic acid (Cone, U. S. 1,584,850), naphthidine (Smith, U. S. 1,627,254), guanidine (Remick, U. S. 1,839,995), indamines and indophenols (Doushkess, U. S. 1,866,400 and 1,916,606), amino-thiazoles (Lenher, U. S. 2,061,632), diamino-thiourea (Smith, U. S. 2,073,762), diamino-diphenyl sulphide (Smith, U. S. 2,073,763), diamino stilbene (Smith, U. S. 2,073,764), various naphthylamines and amino-diphenyls (Simons, U. S. 2,085,675 and 2,085,874), leuco triphenylmethane dyes (Smith, U. S. 2,288,147), and thiazines (Jackson and Parsons, U. S. 2,363,330). Few of these compounds have been used commercially to any extent.

It should be observed in connection with these stain-producing amines that a number of patents have been taken out on the process of applying these compounds to paper in the form of an invisible printed pattern, instead of an all-over coating or as an addition to the beater furnish. In this case, the forger's use of a hypochlorite eradicator brings out a legend or symbol instead of a dark spot. Patents involving such warning legends include Becker (U. S. 1,431,903—"Void"), Neff (U. S. 1,652,042—"Void"), Smith (U. S. 1,675, 769; 1,689,302; 1,817,171—"Void"), Neff (U. S. 1,578,908—"Cancelled"), Neff (U. S. 2,005,105—"Altered") (see also U. S. 2,082,816 (Smith)).

There has, of course, been much research directed toward finding stain-producing materials that respond to more than just hypochlorites. As a matter of fact, any stain-producing chemical to be completely effective should respond to any of the possible eradicators, but as yet no single material is known to have such a wide range of sensitivity. The problem is commonly met by using a combination of two or more chemicals, such as manganese ferrocyanide with one of the amines. However, new materials with an increased range of protection are suggested from time to time, such as mercury or manganese tellurite (Bausch and Schroth, U. S. 2,112,756), iron ammonium cyanotungstate (Schroth, U. S. 2,378,585), and certain benzidine derivatives (Smith, U. S. 2,313,592).

*Mechanical Check Protectors, Indelible Inks, Postage and Revenue Stamps.* Mechanical check protectors (Protectographs, check writers, etc.) and indelible inks have been mentioned in our discussion of generalities and it should be noted that these two devices, when used with care and intelligence, can serve as substitutes for or supplements to a protective paper. The theory here, of course, is that such inscriptions are so permanent that they cannot be altered.

Although check protectors are commonly used, the indelible ink idea has never been popular, in spite of its simplicity, because of the nuisance of keeping a special ink available. The advent of the ball-point pen may possibly change this situation, as with this instrument it is possible to formulate a conveniently usable and really indelible ink. Whether the pen manufacturers will pursue this thought remains to be seen.

Postage and revenue stamps have not been discussed as such partly because the problems of their manufacture and use are not basically different and partly because printing and engraving are the techniques chiefly involved.

For convenience, the bibliography includes separate sections listing domestic patents on postage and revenue stamps and on mechanical check protectors with the thought that those who are interested in these subjects will wish to obtain copies of the entire list. Of the many patents on indelible inks only a few of the more important are given in the list of miscellaneous patents.

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## PART 3—PATENT BIBLIOGRAPHY

The bibliography is divided into the following sections:

1. Authentification methods.
2. Methods of preventing alteration.
3. Mechanical check protectors.
4. Postage and revenue stamps.
5. Miscellaneous related patents.

Each patent listing is accompanied by a one-sentence abstract, except in the sections on check protectors and stamps. These abstracts have been prepared from the original (not from another abstract) and are designed for the use of technical people with papermaking experience.

It is freely admitted that the bibliography is incomplete in some respects, particularly as to foreign patents. Also, a considerable number of patents which are duplicated in other countries are listed only once, especially where the subject matter is of minor interest. There are also bound to be a few errors of omission and transposition in a list of this size.

The patent dates given are those followed by *Chemical Abstracts*, which are the same ordinarily used by the U. S. Patent Office in citing references (*C. A.* 43: no. 1, p. iii, Jan 10, 1949).

### *Authentification Methods*

*United States Patents*

14,069. Combination of inks to prevent photographing or copying. Seropyan, Jan. 8, 1856.

28,370. Characters printed on the middle ply of a three-ply sheet. Howell, May 22, 1860.

34,634. Continuous silk threads which may be colored or treated. Hayward, Mar. 11, 1862.

38,231. Combination of permanent and fugitive inks. Lea, Apr. 21, 1863.

54,834. Printing banknotes on unsized paper and tub-sizing afterward. Jones, May 15, 1866.

54,835. Printing on unsized paper and covering print with thin film. Jones, May 15, 1866.

56,650. Distinctive fibers in localized patterns. Willcox, July 24, 1866.

59,281. Metallic powders scattered in or cemented to the paper. Shaffner, Oct. 17, 1866.

61,321. Continuous threads of thermoplastic material. Crane, Jan. 22, 1867.

66,500. Combination of printing methods to prevent copying. Jones, July 9, 1867.

71,663. Silicate sizing. Sturgeon, Dec. 3, 1867.

137,775. Printing with a combination of reactive chemicals. Jameson, Apr. 15, 1873.

193,221. Bank check with a stub and identification coupon. Brooks, July 17, 1877.

202,515. Stub and coupon for bank checks with concealed identification. Brooks, Apr. 16, 1878.

210,497. Paper colored in stripes on the fourdrinier. Casilear, Dec. 3, 1878.

225,279. Continuous threads colored or treated in segments. Hayward, Mar. 9, 1880.

228,221. Identification marks made with strong caustic. Sangster, June 1, 1880.

282,106. Distinctive fibers of silk, wool, etc., treated with nitric acid. Musil, July 31, 1883.

307,956. Asbestos fiber and colored silk fibers. Jones, Nov. 11, 1884.

447,336. Planchets. Macdonough, Mar. 3, 1891.

481,770. Printed designs in register on face and back. Schlumberger, Aug. 30, 1892.

491,858. "Granite" paper bleached in localized areas. Schlumberger, Feb. 14, 1893.

690,148. A woven fabric with a smooth writing surface. Higgins, Dec. 31, 1901.

711,815. Watermarking with movable rubber type-faces. Behrend, Oct. 21, 1902.

717,799. Process patent corresponding to 711,815 above. Behrend, Jan. 6, 1903.

776,470. Combination of colors and patterns to prevent photo-copying. Ives, Nov. 29, 1904.

776,515. Combination of dyes to prevent photo-copying. Ives, Dec. 6, 1904.

866,293. Invisible legend printed with phenolphthalein. Meyer, Sept. 17, 1907.

964,014. Thin perforated distinctive bands between two plies. Gernaert, July 12, 1910.

1,002,600. Distinctive legend concealed in colored background design. Morris, Sept. 5, 1911.

1,005,696. Label with legend on adhesive side; a protected decal. Czettel, Oct. 10, 1911.

1,299,484. Colorless intaglio ground design under regular intaglio print. Lee, Apr. 8, 1919.

1,428,278. Concealed legend made visible by monochromatic light. Dow, Sept. 5, 1922.

1,457,805. Improvement in geometrical pantograph designs. Woodhull, June 5, 1923.

1,687,140. Watermark in one ply of a two-ply paper. Pleyer, Oct. 9, 1928.

1,737,709. Opaque bank check to prevent tracing of signature. Dwyer, Dec. 3, 1929.

1,822,098. The use of fluorescent substances for identification. Huntress, Sept. 8, 1931.

1,822,148. Naphthoic acids used as in 1,822,098 above. Huntress, Sept. 8, 1931.

1,825,796. Coated paper with distinctive legend under the coating. Himmell, Oct. 6, 1931.

1,899,452. Test chemicals which give several color reactions. Bayle et al., Feb. 28, 1933.

1,929,828. Planchets of metal foil preferably localized in lines. Schlitz, Oct. 10, 1933.

1,938,543. Invisible distinctive fibers sensitive to test reagents. Sanburn, Dec. 5, 1933.

1,990,994. Invisible identifying legend printed with a manganese salt. Lum, Feb. 12, 1935.

1,998,237. Legend under opaque coating; moisture makes legend visible. Himmell, Apr. 16, 1935.

2,019,845. Identifying legend under liner of carton board. Colbert et al., Nov. 5, 1935.

2,021,141. Composition for printing imitation watermarks. Boyer, Nov. 19, 1935.

2,027,741. Invisible pattern rendered legible by moistening. Mackrell, Jan. 14, 1936.

2,048,780. System of printing in multi-colored bands. Clifford, July 28, 1936.

2,067,988. Hidden design developable by action of moisture on chemicals. Smith, Jan. 19, 1937.

2,071,025. Cylinder machine board with differently colored filler plies. Colbert et al., Feb. 16, 1937.

2,083,372. Invisible print of lacquer or gum made visible by moistening. Guthmann, June 8, 1937.

2,119,164. Legend under a surface coating visible by transmitted light. Himmell, May 31, 1938.

2,129,362. Hidden legend developable by application of liquids. Simons and Weiss, Sept. 6, 1938.

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2,129,364. See above. Simons and Weiss, Sept. 6, 1938.

2,143,406. Continuous threads with electrically conductive coatings. Chamberlain, Jan. 10, 1939.

2,143,682. Carton board with filler plies colored in stripes or patterns. Brown, Jan. 10, 1939.

2,180,387. Colored patterns produced by mechanical desizing. Bassford, Nov. 21, 1939.

2,208,652. Cellulose acetate or other ester as a distinctive fiber. Whitehead, July 23, 1940.

2,208,653. Cellulose ester fibers treated to be fluorescent. Whitehead, July 23, 1940.

2,255,696. Fluorescent material in or on paper and protected by a coating. Clifford, Sept. 9, 1941.

2,262,492. Hidden legend under a coating; visible in ultraviolet light. Farrell, Nov. 11, 1941.

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7,462. Background of repeated small design elements. Aulas, 1837.

10,549. Combination of different types of coloring materials. Grubb, 1845.

13,717. Copper soaps to prevent transfer copying. Glynn and Appel, 1851.

760 (prov.). Laminated sheet with plies colored or figured. Loubatieres, 1857.

348. Color combination to prevent photographic copying. Moss, 1859.

3,453. Paper with a fabric facing. Buttner and Will, 1894.

19,963. Embedded marked bands. Corresponds to U. S. 964,014. Gernaert, 1909.

1,084. Designs or legends produced by semi-embossing. Coppier, 1914.

1,136. Use of one design as a halftone screen over another. Farmer et al., 1914.
4,429. Multicolor printing with accurate registration. Morris et al., 1915.
222,779. Paper made with parallel strips of differing composition. Hay and Wiggins and Teape, 1924.
237,828. Distinctive pretreatment of fibers, planchets, etc. Fues et al., 1925.
331,707. Distinctive elements in wavy lines. Johnson, 1930.
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499,438. Distinctive fibers of cellulose esters. British Celanese Ltd., 1939.

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22,573. Proteinaceous fibers colored with nitric acid. Musil, 1883.
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62,052. Treated fibers and over-print reactive to them. Drautz, 1892.
62,053. Multi-color prints in register face and back. Drautz, 1892.
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243,972. Laminated board with differing plies. Dittmar, 1912.
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283,752. Color applied to wet, freshly-formed paper web. Luttich, 1915.
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446,656. Engraving procedure. Nefgen, 1927.
487,824. Perforated or printed web embedded in sheet. Gernaert, 1929.
497,037. Fluorescent materials in or on paper. I. G. Farben. A.-G., 1930.
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85,401. Printing method with special line screen. Hazura and Aufreiter, 1921.
92,282. Chemical identification test (for genuineness). Ehrlich, 1923.
125,578. Colored watermarks. von Heinrich, 1931.

***Methods of Preventing Alteration***

*United States Patents*

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27,857. Figures or designs printed inside a two-ply sheet. Carey, Apr. 10, 1860.
38,835. Similar to 4,143 but outer plies containing a filler. Olier, June 9, 1863.
53,081. Ferrocyanides for ink-fixing and for warning stain. Loewenberg, Mar. 6, 1866.
84,341. Preventing the addition of new digits to printed numbers. Casilear, Nov. 24, 1868.
101,786. Paper colored with any fugitive dye. Thomae, Apr. 12, 1870.
105,125. Paper tinted with silver compounds. Price, July 5, 1870.
115,005. Paper tinted with at least two differently sensitive dyes. Willcox, May 16, 1871.
121,946. Application of sensitive dyes in the size tub. LaMonte et al., Dec. 19, 1871.
123,782. Tinted patterns formed in the size tub. LaMonte and Saxe, Feb. 20, 1872.
125,550. Background design ruled in writing inks of various colors. Duthie, Apr. 9, 1872.
167,223. Paper faced with a thin woven fabric. Casilear, Aug. 31, 1875.
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227,559. Tannin to permanently fix ink writing. McMahon and Wyman, May 11, 1880.
237,746. Different fugitive tints in the sheet and on its surface. Hendrichs, Feb. 15, 1881.
243,342. Paper containing iron and tannin; water causes reaction. Ford, June 21, 1881.
246,100. Combination of heavy metal salts and sulphides for warning stain. Dupre, Aug. 23, 1881.
248,198. Combination of differently sensitive dyes. Nesbit, Oct. 11, 1881.
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302,758. Iodides, iodates and manganese or lead salts. Menzies, July 29, 1884.
305,292. Printing with an iron gallo-tannate ink. Clapp, Sept. 16, 1884.
322,130. Barium chromate and indigo. Schreiber, July 14, 1885.
322,131. Lead ferrocyanide to produce warning stains. Schreiber, July 14, 1885.
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531,507. Combination of iodides and fugitive dyes. Carvalho, Dec. 25, 1894.
538,625. Permanent and fugitive colors printed in close registry. Robertson, Apr. 30, 1895.
547,289. After-treatment applied to written bank checks. Remke, Oct. 1, 1895.
595,281. Permanent and fugitive colors printed in close registry. Yetter, Dec. 7, 1897.
630,255. Making ink writing permanent by carbonizing with heat. Morrow, Aug. 1, 1899.
643,084. Paper sensitized with alkaline indigo. Colgrove, Feb. 6, 1900.
774,535. Soluble ferrocyanides, iodides and iron salts Rowan, Nov. 8, 1904.

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894,664. Watermarks and coupons to limit value of bank checks. Kimber, July 28, 1908.

953,081. Fugitive tint covered by a translucent coating. Wilson, Mar. 29, 1910.

967,793. Sensitive colors printed with an albumen-type vehicle. Lorenz, Aug. 16, 1910.

967,794. "Fixing" sensitive colors on paper surfaces. Lorenz, Aug. 16, 1910.

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1,390,959. Bank check with background and imprint fugitive. Longmesser, Sept. 13, 1921.

1,417,820. Dark colored paper with white coating. Goodman, May 30, 1922.

1,431,903. Warning legend obscured by fugitive over-print. Becker, Oct. 10, 1922.

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1,454,837. Warning legend obscured by design in fugitive ink. Smith, May 8, 1923.

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1,535,861. Benzidine as a source of warning stains. Sammet, Apr. 28, 1925.

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RECEIVED Dec. 22, 1949. Presented at the Annual Meeting of the Technical Association of the Pulp and Paper Industry, New York, N. Y., Feb 20–23, 1950.

# RAW STOCK FOR COATED PAPERS

***Papers Presented at the Second Coating Conference, Boston, Mass. April 18–20, 1951***

## Specifications for Manufacture and Conversion of Hanging Paper

THOMAS F. LA HAISE

STATISTICS indicate that the production of no. 2 hanging paper ranges from 100,000 to 130,000 tons per year from which is manufactured approximately 300,000,000 to 400,000,000 rolls of wallpaper annually.

Specifications on no. 2 hanging paper have been somewhat vague, and it is the intent of this paper to outline a tentative set of specifications and clarify them as correlated to the actual production and conversion of hanging paper into wallpaper with the hope that it will instigate further investigations and modification of these specifications.

**Specifications for No. 2 Hanging Paper**

| | |
|---|---|
| Basis weight: | 9 oz.—38 lb. 24 × 36—480, range 37–39 lb.<br>10 oz.—42 lb. 24 × 36—480, range 41–43 lb.<br>12 oz.—50 lb. 24 × 36—480, range 48–52 lb.<br>14 oz.—58 lb. 24 × 36—480, range 56–60 lb.<br>16 oz.—66 lb. 24 × 36—480, range 64–68 lb. |
| Tear factor: | 60–65% M.D.; 75–80% C.D. |
| Burst factor: | 25 to 30% |
| Porosity or density: | 15 to 30 seconds |
| Sizing: | A. Ink penetration; 3 minutes minimum. 4 to 6 minutes preferred<br>B. Cobb test; 0.25 gram maximum |
| Dirt: | Free as possible from shives and large wood dirt. Free from "oily" spots, such as slime, oil, wax, size spots, etc. |
| Color: | Minimum of 57 brightness |
| Caliper and finish: | Moderate machine finish, all available bulk, free from markings |
| Moisture: | 6.0–6.5%. Uniformly dried |

These specifications were determined after extensive plant investigations over a period of years in a small paper mill where no. 2 hanging is made exclusively and converted into wallpaper in another division of the same company. The paper characteristics were varied intentionally, and the effect of these variations observed on the wallpaper converting machine operations, coating adaptability, and ultimate application to walls where possible.

### GENERAL DISCUSSION OF SPECIFICATIONS

#### *Weight*

A variation of 3% is allowable, but variation in excess of this amount is objectionable. Weights below standard usually have lower strength characteristics. Weights above standard reduce yield of wallpaper rollage per ton.

#### *Tear Factor*

The tear factor is controlled principally by percentage of unbleached sulphite, or semi or bleached sulphate in the furnish, usually ranging from 15 to 30%.

Tear factor is most important for converting machine operation. As tear factor drops below specifications, operating efficiency of converting machine decreases because of edge tears in the paper which cause breaks and stop-offs. Cross-direction tears usually start where coated paper is pulled from the sticks on festoon racks at the end of the drying rack and cause breaks on the print machine, reels, or rolling machines.

Tear factors of 70% C.D. are suitable for converting machines operating at relatively slow speed of 600 to 700 rolls per hour, but 80% is required for higher speeds of 1200 to 1300 rolls per hour.

Tear factors higher than 80% are required under certain conditions, and would be desirable, but economics of increased sulphite consumption must be considered.

Paper made with tear factors as low as 60% has been hung by paper hangers without complaints, but specified tear factors assist materially in preventing general hanging complaints.

#### *Burst Factor*

The bursting strength is controlled principally by the strength of the groundwood. Strength usually varies with the freeness of the groundwood and care must be taken not to lower the freeness too low and increase amount of fines as it varies porosity to a point where it is more detrimental than advantages gained by a high burst factor.

Variations of the burst factor have very little effect on converting machine operations or coating adaptability, but factors below 25% increase hanging complaints from the paper hangers.

#### *Porosity or Density*

Porosity is controlled principally by the freeness of the groundwood with porosity decreasing as freeness increases. Porosity should not exceed 30 seconds on any weight, but it is most sensitive on 9-ounce (38 pounds) where porosity should not exceed 25 seconds, and 15 to 20 seconds is preferred.

Variations of porosity have considerable effect on converting machine operation, coating adaptability, and hanging characteristics.

Porosities above 25 seconds result in the paper cockling on the coating machine jacket, curling on the drying rack causing stick edges which in turn result in tears and stop-offs. The paper also curls badly on pasting and results in complaints from paper hangers.

Paper with a porosity below 15 seconds further improves lay of paper on coating machines but has a tendency to cause mottled coating and requires higher coating weights to obtain coverage.

#### *Sizing*

The ink penetration test is controlled principally by amount of rosin size, usually 1.5 to 3.0% of furnish, combined with alum and sodium aluminate.

Variation of the ink penetration test between 3 and 10 minutes does not affect converting machine operation and has but slight effect on coating adaptability. Paper with a 1 to 3-minute test operates satisfactorily on converting machines, but coating adaptability is reduced slightly.

Complaints from paper hangers of hanging difficulties and paste penetration are increased when ink penetration tests

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are 3 minutes or lower. Ink penetration tests of 4 to 6 minutes and even higher are recommended to reduce paperhanger complaints.

The Cobb test does not follow ink penetration tests but is usually 0.20 gram or lower when ink tests are above 4 minutes and generally increases as the ink penetration test drops below 4 minutes.

Cobb tests above 0.30 gram and with both high and low ink penetration tests decreased coating adaptability and resulted in numerous complaints from paper hangers.

A maximum Cobb test of 0.25-gram and maintenance of test as close to 0.20 gram is recommended.

***Dirt***

Specifications are rather vague, but dirt count is not too indicative.

Amount of shives and large wood dirt specks is controlled by a grinding and screening process.

Numerous shives cause mottled coating, and large wood dirt is difficult to coat and sometimes requires additional coating weight to prevent complaints from consumers.

Dirt spots caused by "oily" spots such as slime, oil, wax, size spots, etc., must be avoided at all times. These spots are very difficult to detect in the raw stock as they are very similar to fine wood dirt, but when they are coated, the coating acts like an absorbing material and draws the "oily" substance from the spot, and the result is a large translucent ring in the coating with a pronounced core, and the net result is considerable amounts of damaged wallpaper.

The occurrence of these "oily" spots is controlled and eliminated by the following methods:

*Slime Control.* Continued controlled use of bactericides such as chlorine, chloramines, chlorphenates, and mercurials. In over 80% of cases where "oily" spots appear in the paper, slime build-up was found, either generally or locally, in the system, mostly in the groundwood system, and when cleaned-up spots were eliminated. Slime may not be directly the cause of these spots, but whenever slime is apparent there is imminent danger of these spots occurring.

*Stock System Clean-Ups.* Systematic and organized clean-ups of the entire stock system are a must to eliminate these spots.

"Easy to get at" places are usually cleaned, but it is the "hard to get at" places that are usually neglected and are a source of contamination.

Proper design of the system is imperative for a clean system. Use of uncoated wood or non-ferrous metals must be avoided in flow boxes, pipes, and chests. All dead spots or low velocity flows should be eliminated. Flow boxes and chests should have easy to get at clean-out openings and should drain readily. Pipe installation should be designed for easy inspection and cleaning. Dead-end fittings and pipe branches that have been "temporarily discontinued" should be eliminated.

*Eliminate Possible Sources of Oil Contamination.* A systematic survey of the oiling system should be made with intent of eliminating possibility of oil entering the stock system.

A few examples are the replacement of oil-lubricated bearings on grinders, deckers, presses, or plunger pumps with water-lubricated bearings, and the installation of proper drip pans on bearings on shafting over open stock systems.

Enough emphasis cannot be placed on a system free from contamination and any investment made in improving the cleanliness of the system will pay dividends by reducing or eliminating the loss incurred by production of damaged paper caused by these "oily" spots.

Some investigations have been made on methods of observing these "oily" spots during inspection of the paper but to date there is nothing concrete to offer except that a large majority of the spots that occur in the coated paper fluoresce under "black light," and it is hoped that its use can be developed into a practical method of detecting these spots in the paper before coating.

***Color***

A G.E. brightness of 57 is specified as this is the average brightness of groundwood. A higher brightness is desirable. A good percentage of wallpapers are coated with a fairly deep tint and brightness of the paper is not a factor, but on the lighter tinted and white coatings, coating weights must be increased, and more expensive clays or pigments used in the coating as brightness decreases.

Permanency of the brightness would be a more desirable factor as coating weights must be maintained primarily for light-fastness.

***Caliper and Finish***

Moderate machine finish with all available bulk possible with groundwood is desirable. Bulk is important on heavier weights that are embossed.

Finish should be sufficient to prevent mottled appearance of the coating, but improved finishes obtained by finer felts and more calendering did not appreciably improve appearance of coating.

Finish includes not only the over-all smoothness of the sheet, but also localized markings impressed in the coating side of the paper after it is formed and pressed.

Frequent causes of markings are a rough drier canvas or one filled with foreign material, such as pitch or size, and also seam markings caused by sewed, glued, or clippered seam. Build-up on the drier surface will also cause marking. All of these markings distort the coating and result in damaged wallpaper.

Corrective measures are clean, endless drier canvas and doctored driers.

***Moisture***

A moisture content of 6.0 to 6.5% is specified as under 6.0% the sheet becomes more brittle and susceptible to tears on converting machines, and above 6.5% the drying of the coated paper is impaired slightly.

Uniformity of drying is most important. Uneven drying across the sheet causes slack edges that result in slack draws on the coating machines and causes skips in the coating and misprint on the print machines. Forced drying with uneven moisture throughout the sheet causes cockling on the coating and print machines and results in brush marks, color skips, and misprints.

As stated at the introduction of this paper these specifications are general and subject to modification and improvement, but they have been applied for the last few years with good success in one mill, and it is believed they could be used generally to the satisfaction of many wallpaper manufacturers.

# Basic Desirable Qualities of Boxboard for Off-the-Machine Coating

A. T. LUEY

The application of clay coating to boxboard is currently being accomplished by many ways, both on and off the machine. "Off-the-machine coating" is the term commonly applied to a process which coats the board after it leaves the paper machine.

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The desirable qualities of boxboard to be coated in this manner are naturally closely related to some of the specifications of the finished board, and the coating material applied will alter the board to meet other specifications.

This paper is limited to a discussion of the desirable qualities of the body stock for off-the-machine clay coating which can be classified as follows:

1. Appearance.
   (a) Cleanliness—absence of spots.
   (b) Brightness.
   (c) Formation.
   (d) Smoothness.
2. Functional and basic qualities.
   (a) Bender.
   (b) Ply bonding strength.
   (c) Caliper uniformity.
   (d) Basis weight uniformity.
   (e) Proper moisture content.
   (f) Sizing.
   (g) Curl.

## APPEARANCE

### *Cleanliness*

Normal coating weights applied to boxboard in off-the-machine coating will be 6 pounds per thousand square feet and, at times, it will go as high as 8 to 9 pounds. Because of this it is possible to have a top liner that is quite dark and not free of shives and spots as would be required for machine coatings using light coat weights. The severity of the spots that can be tolerated is dependent on the coat weight and opacity of the coating (*1*).

Spots that will bleed, such as asphalt, are very objectionable since they frequently will not come through to the surface until the stock is 2 or 3 weeks old. This type of defect will frequently cause trouble even if the foreign material is located in the filler. Because of this the waste paper used in the furnish should be carefully selected with this in mind.

### *Brightness*

From an economical standpoint it is much less expensive to obtain a high white sheet by the application of a heavy coat weight, bleached clays, etc., to a relatively dark sheet than to keep the coat weight down and use a relatively white top liner. The ability to apply a heavy coat weight is one of the cardinal features of "off-the-machine coating" and it should be fully exploited here because of the economical factor.

A typical top liner furnish would consist of 25% unbleached sulphite pulp, 50% sulphite waste papers, and 25% groundwood waste papers. The total ash of the mixture will frequently run as high as 12% due to the heavy loading of the waste papers. Variations in this furnish will be necessitated by the current prices of pulp and waste paper, the ability of the beater room to properly process waste papers (deinking), and the quantity of virgin pulp required in combination with the particular grades of waste paper used to produce a good bending board.

### *Formation*

A uniformly formed top liner is essential to prevent "shadow" show-through due to brightness variations across the sheet. This is of decreasing importance when underliners are used (*2*).

### *Smoothness*

The smoothness of the final coated board is closely tied to the smoothness of the body stock. Wire marks and felt marks that appear slightly on an uncoated board will seem quite pronounced on a coated board.

Usually a water box at the calender stacks is sufficient to lay the fuzz and smooth the sheet although some mills find that a size press is an additional advantage. The water box treatment should contain enough starch to lay the fuzz and wax emulsion to prevent any picking of the starch on the stacks. The water box treatment should also produce a down-curl to the sheet to compensate for the up-curl produced by the coating.

## FUNCTIONAL AND BASIC QUALITIES

### *Bender*

The application of coatings, especially of heavy weights, will aggravate bending problems and as a result, body stock for coating must have excellent bending qualities. This feature is also closely related to the final moisture content of the coated board which must not be overdried (*3*).

### *Ply Bonding Strength*

The internal bonding strength of the board between plys and the strength of the top liner must be satisfactorily high. This is a characteristic that should apply to any grade of board but it is especially important for coated board since so many orders are printed with gloss inks, varnishes, or printed by offset methods (*4*, *5*).

Borderline failures in this class are frequently blamed on improper coating instead of the board.

### *Caliper Uniformity*

High and low caliper spots will result in an uneven, mottled appearance of a coated sheet after the supercalenders. The whole sheet must be as free of caliper variations as possible. In addition, undefibered lumps of pulp and paper in the sheet will produce objectionable "shiners" on calendering.

### *Basis Weight Uniformity*

This will be closely related to the qualities mentioned in relation to caliper uniformity. The finishing room, in an effort to maintain a uniform caliper, will be forced to change the operating pressures on their supercalenders to compensate for variations in basis weight. This will result in variations in smoothness of the finished board.

### *Proper Moisture Content*

It is very important to maintain the correct moisture content, approximately 6%, of the coated board. If it is too high the sheet will blacken at the supercalenders, and if it is too low the board will lose bending qualities.

The uncoated board should be maintained at a uniform moisture content within the normal range in order to facilitate the maintenance of a uniform moisture content of the coated board.

### *Sizing*

The degree of sizing of board to be coated has often been a subject of discussion. However, experiments by the writer have failed to show any measurable difference in coated board over wide ranges of sizing. No tests were made on board having a water drop test less than 15 seconds, and it is quite possible that board slacker sized than this would cause problems (*6*, *7*).

### *Curl*

The application of coating produces an up-curl and to offset this the body stock should have a down-curl.

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# Coating Raw Stock for Off-Machine Book Papers

A. LEWENSTEIN and P. B. HANSEN

Of the three elements that enter into paper coating, the machine, the coating color, and the body stock, the last named can be, and often is, the most troublesome to the coater. While the coater has control of his machine and can control within fairly close limits the character of his coating, he has little control over the manufacture of the body stock. The coater, therefore, establishes a set of specifications which he hopes will describe the kind of paper he needs, and the papermaker attempts to meet these specifications. Unfortunately for both, this ideal of setting up a set of standards to satisfactorily describe a good sheet of coating raw stock has not yet been completely realized. The papermaker has many tests which tell him a good deal about the paper he is making. They do not tell him enough about his product as raw stock for coating.

This paper will attempt to assess the present state of knowledge of what is necessary and desirable in coating raw stock, to consider the various means of paper evaluation, determine their degree of applicability to coating raw stock, and to point out possible avenues of research that might result in improved means of predicting raw stock performance.

In general terms, the properties thought necessary in coating raw stock are:

1. The ability to go through the coating process and remain relatively flat. Paper which tends to curl excessively, cockle, or become otherwise badly distorted when the coating is being laid down causes numerous troubles, among which are streaks in the coating and breaks during calendering.

2. Paper which is to be coated one side only should not curl excessively when being coated and should result in a product which stays flat in the print shop and does not give trouble when used as, for instance, labels. Either coated one side or coated two side papers should undergo minimum and uniform change in dimensions when subjected to changes in moisture content.

3. It should be possible to apply coating to the base paper and obtain a level, continuous coating which can be calendered to produce a surface of uniform gloss and good printability.

4. It should be possible to bond the coating to base paper and obtain the right *kind* of bond without using excessive amounts of adhesive.

5. Brightness should be high enough to give the final brightness desired with the coating colors to be used.

6. The raw stock needs to have sufficient strength to withstand the stresses applied to it in coating, and during final use. Important among these are:

(a) Sufficient wet tensile to go through the long draw of a double coater.
(b) Resistance to splitting when printed by offset lithography.
(c) Correct rheological properties to withstand high-speed printing operations.

In attempting to augment their knowledge of coating raw stock the authors have surveyed the available literature (which turned out to be relatively scanty), and have made a number of personal contacts with people active in this branch of our industry. These conferences emphasized the uncertainty that most people seem to feel about evaluation of raw stock and brought out that there are many differences of opinions on the usefulness of various tests. There is agreement on one point, however, and that is that uniformity of properties is a highly desirable quality. It will probably also be agreed that the properties of the sheet should be the same in all directions, that is, that the machine direction and the cross-direction characteristics should be the same and that the character of the felt side be the same as the wire side. In practice both uniformity and equality of directional characteristics are difficult to achieve.

With specific reference to the problem involved in manufacture of a sheet that will lie flat on coating and give a minimum of trouble with curling, let us consider the question of uniformity. Friel (*1*) shows that when the variation in basis weight and air porosity (Gurley densometer reading) exceed certain values the base stock will curl and buckle and will wrinkle at the coating machine reel. Friel expresses his data in terms of what he calls "uniformity factor" which is the result of an arbitrary treatment of basis weight and density variations.

The work was done chiefly on paper in the basis weight range of 44 pounds (25 × 36—500). Friel states that the same tendency exists also in heavier papers, but that much greater variations can be tolerated.

Frost and Russell (*2*) give additional evidence of the dependence of good performance on minimum variability in basis weight. They claim that opacity variability is a good indication of basis weight variation. Transparent areas are relatively light in weight and low in density. Dark areas are heavy and of greater density. These authors show that a maximum variation in opacity of 2% will give no trouble. Variations of 2 to 3% will not give trouble if the maximum and minimum weights are not close together. Variation in opacity of 3% or more will nearly always result in trouble. maximum distortion generally occurring at the point of most rapid opacity variation.

It should be made clear that the type of variation being considered here is not discoverable by the routine methods of determining basis weight, opacity, and density usually used in controlling the process of papermaking. These workers found it necessary to make many individual tests on samples representing the entire widths of their machines, a procedure which, with existing apparatus, would be entirely impractical from an operating point of view. The apparent significance of their results points up the desirability of having available instruments which will permit one to obtain quickly a record of significant paper properties measured at adjacent points in a fairly long or large sample of paper. The recently developed beta gage (*3*) may have considerable application here.

Consideration of the distortions to which paper is subject, especially with reference to coating, inevitably leads one to be concerned with the effects of wetting paper with water and subsequent redrying. A few observations and suggestions

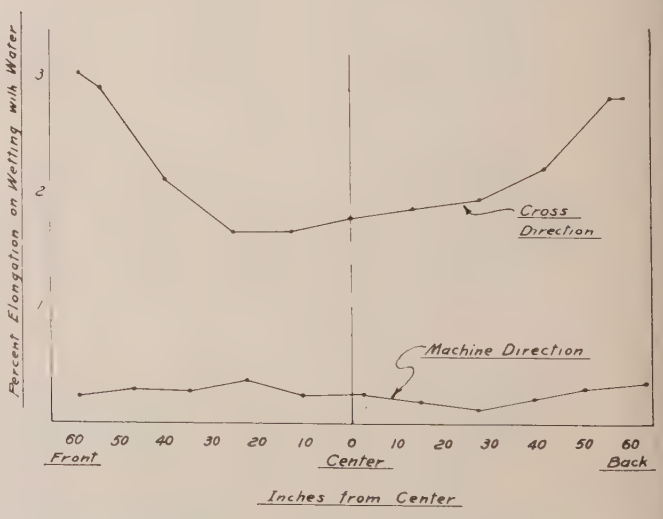



***Fig. 1. Elongation of paper specimens from different points in sheet when saturated with water***

A. Lewenstein, Chief Chemist, Appleton Coated Paper Co., Appleton, Wis.
P. B. Hansen, Technical Director, Bergstrom Paper Co., Nennah, Wis.

of this point may be in order. It is, of course, well known that paper changes its dimensions when moistened, the cross-direction change always being greater than the machine-direction change. It doesn't seem to be so well recognized that the cross-direction swelling is not uniform from edge to edge of the sheet as delivered from the paper machine, but passes through a minimum at the center. This effect has been referred to by Bialkowsky and Probst (*4*). Some work carried out by the authors shows the character of the effect. Figure 1 shows typical results.

This characteristic of wet swelling seems to be connected with other properties of paper. For example: the cross-direction tensile strength not only differs greatly from machine-direction tensile, the cross-direction tensile itself also varies as one goes from edge to center of the sheet. For a comprehensive treatment of the subject, one is referred to Steenburg on the subject of paper as visco elastic body (*5*). Recent work suggests that all these effects have a common origin. Edge (*6*) and Rance (*7*) have given convincing evidence that stretching of the sheet while wet (due to draws in the paper machine) together with drying under tension, are at the root of these characteristics. Concerning tension drying, Rance says:

"These findings are of the highest significance with regard to the fundamental causes of the wet expansion of the paper web and of the anisotropy of this characteristic. The evidence is consistent with the suggestion that in a loosely felted planar mat of cellulose fiber there is, on drying, a considerable amount of twisting and kinking of the fibers which tends to shrink the mat into a condition of greater density. On this view the shrinkage of the wet web may be visualized as due to a twisting, coiling up, and shrinking of all the fibers of the sheet, a phenomenon associated with, but not directly caused by, the lateral shrinkage of the individual fibers. In the machine direction the tensions prevent or hinder this kinking effect and the fiber-to-fiber bonds are made while the structure is under tensile restraint. In the cross direction there is freedom from shrinkage of the web and the fibers can twist and kink without restraint.

Van den Akker (*8*) has suggested that some of the phenomena of hygroexpansivity of tension dried paper may be partially explained by the existence of frozen-in stresses in individual fibers, and the tendency of these fibers to revert to their natural configurations when moisture content is increased. Presumably, fibers which had been allowed to kink and twist on drying would relax and stretch out while fibers which had been stretched to more than their normal straightness might assume somewhat contorted configurations. The first effect would apply to that component of fiber orientation lying in the cross direction, the second to that lying in the machine direction. Since relatively unhindered shrinkage was allowed in the cross direction while drying, it could be expected that the spring-back in this direction would be much greater than that in the machine direction, in which direction the sheet was constrained to retain its initial length. The functional relationship between cross-direction swelling and distance from sheet center is consistent with these ideas because it is reasonable to suppose that at and near the edges of a sheet there is unlimited opportunity to shrink, but at points closer to the center, the tendency of the sheet to grip the drier restrains shrinkage.

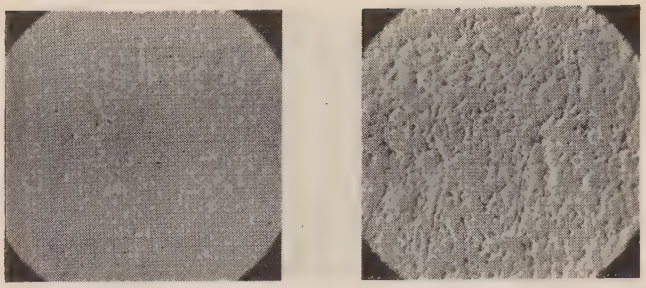
How can these considerations be applied to explanation of sheet distortion, discovery of its basic causes, and manufacturing control? It seems necessary to add one more point to those made in the preceding paragraphs. That point is that in addition to the different *average* restraints to shrinkage in the cross direction and machine direction, there are *localized* restraints which may act in either direction. Thus, we could conceive a situation in which fibers in one sheet area would have been subjected to a greater or lesser straining than fibers in a contiguous area. Hence, these areas would exhibit different swelling characteristics when dampened, and the result would be distortion. Because of the difference in the histories of the two areas their behavior on redrying would also be expected to be different resulting in permanent distortion.

It seems that localized differences such as those mentioned could develop as a result of variations of basis weight. Light areas could be thought of as drying more rapidly than the heavier areas resulting in a greater degree of frozen-in stress than the light areas, hence, differences of behavior on wetting. The work of Friel, Frost, and Russell therefore, while not elucidating the fundamental causes of sheet distortion may provide a good starting point for development of mill control methods.

In the conversations already alluded to sheet density (Gurley densometer) was frequently mentioned as the one quality that could be measured that seemed to provide some basis for predicting paper performance on coating. The consensus seemed to be that by and large the least dense papers performed the best. Some people indicated that the density should be run just as low as possible and still have the sheet possess proper strength qualities, especially resistance to splitting. This seems consistent with the points made concerning the effects of localized areas of varying fiber strain (or frozen-in stress).

The coater and printer alike experience the greatest trouble with curling when paper undergoes a change in moisture content. Reed (*9*), in discussing the curling of lithographic papers, refers to paper grain, two-sidedness, density, and unrelieved stresses as being separately or collectively the basic causes of curling. He also claims that increasing the moisture content of a sheet to 9% or above will result in stress relief (fiber relaxation). If one side of a sheet is brought to this moisture content but not the other the sheet can be expected to curl. This condition arises in coating paper one side at a time. Why do some sheets curl and others not? Experimental evidence indicates that fiber orientation of felt and wire sides of a sheet can vary rather widely. Whenever such differences exceed certain limits a sheet is produced which is likely to curl, and this type of curl will be difficult to control.

One of the primary purposes of coating is to obtain a level surface on which to print. While properly applied coating, especially in the heavier weights, always does improve the levelness and printability of paper, there is much that coating cannot level out or cover up. Among the base stock defects that cannot be successfully eliminated are wild formation and fuzz. These are obvious faults readily seen by the papermaker and need not be elaborated here. There are at least two other attributes of base stock which strongly affect the nature of the coated surface and which are not so readily apparent to the papermaker. The first of these can only be described subjectively. The practical coating man speaks of it as "the way the paper takes the coating" and describes it in approximately the following terms: good base stock is uniformly and evenly wetted. The coating levels out on it completely. The liquid portion is absorbed by the base stock at the proper rate. He is more apt to criticize paper because it absorbs too slowly rather than too fast. By way of example he may state that base paper containing a high percentage of groundwood fiber practically always has these desirable qualities while a raw stock composed of all new sulphite fiber which has been highly hydrated, hard sized, and heavily calendered is most likely to lack them. The latter is apt to have a surface which after coating will have areas variously known as "spots," "fisheyes," "birds eyes," or "grease." The latter term is probably the most descriptive. The paper acts *as if* there were areas on it which were greasy and could not be wetted by the coating. These extremes are easy to describe; the reasons for their existence, hard to explain. What is still harder to explain is why a given set of apparently uniform papermaking conditions adjusted to operate far from either extreme will produce paper with ac-



a b

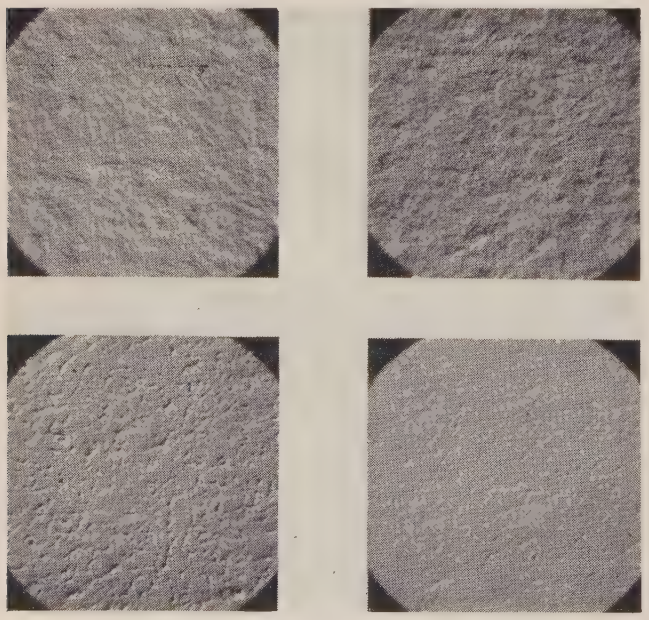
***Fig. 2. Extreme case of pebbly coating***

Valley sizing: a: 51 sec. b: 13 sec.

ceptable properties in perhaps 95% of the time and unacceptable the other 5%.

The wettability of the paper surfaces had been studied by Knight (*10*). The principle of the method he used is to rapidly apply a colored solution to the paper and remove it a small fraction of a second later. Various stain patterns are obtained, some uniform, others extremely nonuniform. Modifications of this method have been used by some coating mill laboratories with similar results. The reasons for these differences remain obscure. Anyone long associated with the coating industry has almost certainly had his share of trouble with inability to lay down a smooth coating on a given raw stock and will agree that further work along this line is highly desirable.

The other attribute of base paper which affects the nature of the coated surface can only be described by the result it produces. This result is variously termed "orange peel," "egg shell," or "pebbly" surface. What is meant is a coated surface which, instead of being more or less level and continuous, is rough and discontinuous as if composed of tiny pebbles. Any type of coating may produce this result on different lots of the same grade of base stock. It may even happen that paper from one continuous run on the paper machine when coated under test conditions will show all degrees of pebbliness from barely perceptible to severe. The following set of photomicrographs illustrate this phenomenon. Figure 2, a and b, shows an extreme case. These are photographs of the surfaces of two papers coated under identical conditions with the same coating. The raw stock is the same grade but comes from two different mills. Figures 3 and 4, a and b, are photographs of the surfaces of uncoated and coated stock. The stock is all from one continuous machine run. Figure 3 shows felt side, Figure 4 wire side. In each figure the left-hand pair is on slack-sized paper, the right hand is hard. The actual values are shown under each figure.



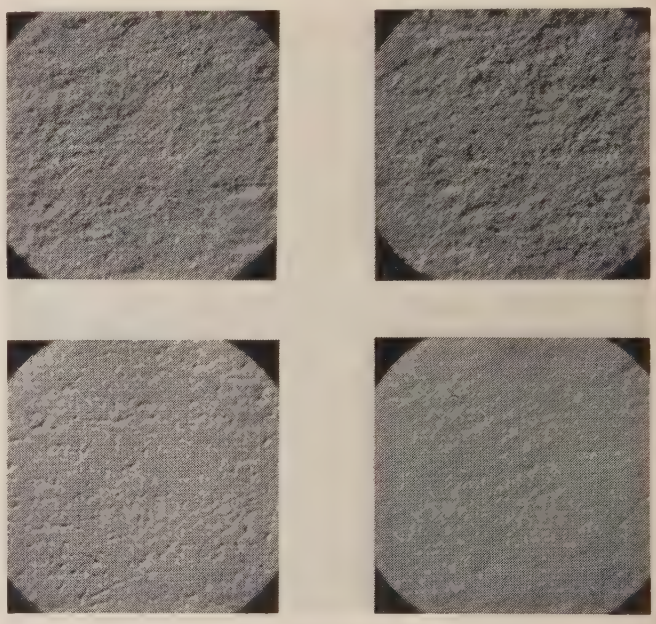
a b

***Fig. 3***

Valley sizing: a: 11 sec. b: 71 sec.

The bond between coating and base stock is a subject of greatest concern to the coater. Traditionally the strength of this bond was expected to be high enough so that if and when failure occurred it would always be in the base stock, not within the coating or at the coating paper interface. The coater assumed that the tensile strength of the body stock normal to the surface would always be high enough to resist all printing stresses. This assumption is not always justified, but for the purpose of discussing coating to raw stock bond, we shall accept this assumption as valid.

Frequently the coater finds that on certain runs or parts of a run of base stock he must increase the ratio of adhesive to coating in order to maintain the type of bond described earlier. For casein or soya protein this increase may range between 6 and 18% of the original. Occasionally it is found that increases of adhesive as high as 30% will not produce the desired type of bond on certain raw stocks. Aside from being expensive such additions of adhesive lower the brightness and gloss of the coating and detract from its printability. This is not to say that the additions of adhesive do not produce an increase in resistance to picking. They do. But the increase does not seem to be proportional to what is obtained on good raw stock. Furthermore, failure, when induced by any means, continues to take place at the paper coating interface. While paper with this kind of bond may be successfully printed the chances of its picking are much greater than with paper having the desirable type of bond. Picking is almost sure to take place if the paper is even slightly kinked.



a b

***Fig. 4***

Valley sizing: a: 12 sec. b. 73 sec.

The following mechanism to account for the particular type of failure of coating bond just described is based on Singleterry's (*11*) idea of the existence of a zone of weakness a micron or two away from the coating-paper interface on the coating side. Singleterry's idea is best illustrated by his "Schematic Graph for Tensile Strength Relations in a Coated Paper" reproduced in slightly modified form in Fig. 5 from his original article.

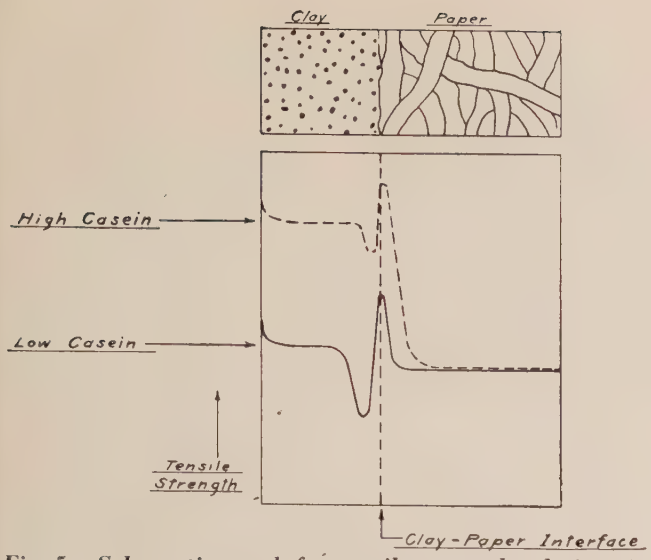



***Fig. 5. Schematic graph for tensile strength relations in a coated paper***

When an aqueous coating consisting of a finely divided pigment and an adhesive in true or colloidal solution is applied to paper there is first an immediate migration of water into the body stock. This carries some of the adhesive with it. If the coating is being dried on a modern drier in 15 seconds or less the rate of travel of water toward the surface is high enough to concentrate a perceptible amount of adhesive at the surface. Both actions tend to rob adhesive from the interior of the coating and produce a zone poorer in adhesive than either the region next to the base stock or the surface of the coating.

Theory indicates, practice confirms, that this zone of weakness when great enough to be perceptible is most often found near the coating paper interface.

Dappen (*12*), working with starch-sized coatings, found that between 3 to 4% of the starch in a coating penetrates into the base paper. He also found that a coating when applied to glass shows a marked increase in concentration of starch at the surface and a decrease at the glass interface, especially when dried rapidly. Similarly, filter cakes of coating when dried showed strong redistribution of starch, a zone near the bottom of the cake and another at the top having more than the original concentration while the center had less. Dappen did not find a similar redistribution of starch in coating applied to paper and air dried. However, he recognizes that his technique was not able to establish the starch concentration at the critical raw stock coating interface. In his theoretical discussion, Dappen fully recognizes that his work implies support of Singleterry's concept.

Casey and Libby (*13*) studied the penetration of starch adhesive into the base paper by staining with iodine cross sections of coated sheets. They found that increasing the density by beating and increasing the amount of rosin size decreased the penetration of the starch into the base stock. Alumina also was partly effective in decreasing penetration.

A large number of practical observations and empirical tests made by the authors over a long period of time indicates that the ability to bond a given coating to base stock varies through wide limits with different runs of the same grade of base stock. Casey and Libby's work would seem to indicate that density and sizing are of governing importance in the nature of coating to raw stock bond, and well they might be. The authors would like to bring to attention a discrepancy often found between results obtained in coating certain base stocks the manufacturing history of which is known and other stocks, the history of which is not known but whose measured properties do match the known base stock. For example, Casey and Libby found that increased beating reduced depth of starch penetration and so did addition of rosin size. They recorded the Gurley density of their handsheets and were able to demonstrate a relation between densometer reading and depth of penetration. The authors' experience based on numerous observations is that, starting from the position of the receiver of raw stock who does not know the manufacturing history but tests it for conformance to specifications, Gurley density and sizing as measured by several methods do not correlate well to the nature of bond obtainable.

The authors' conclusion is that, for the present at least, the only way to find out anything about the nature of bond obtainable on a given raw stock or the kind of surface that will be obtained is to coat it. It is suggested that a standard test be worked out which could be used to control the manufacturing process. If control is too much to be hoped for, then a test like this would at least furnish dependable information that could lead to control.

We have referred to the requirement that paper must be able to withstand press stresses. It is in order to point out that in printing, paper is subjected to high stresses and that these are applied very suddenly. The magnitude and rate of application of tensile stresses normal to the surface of the paper determine its tendency to split. The ability to deform elastically as well as its tendency to flow and take permanent set under these conditions (its rheological characteristics) determine how the paper will perform. This has been indicated by the work of Rance, Steenberg, et al., already referred to, who have shown that the rheological properties of paper rather than ultimate strength as commonly measured determine its performance.

Until comparatively recently, methods of measuring resistance to splitting have been unsatisfactory, but encouraging progress is being made in this direction. The Davidson instrument (*14*) tests resistance to splitting under reproducible conditions of printing speed and ink viscosity. A very promising development is the instrument evolved at the Institute of Paper Chemistry (*15*). This instrument makes it possible to express the splitting in terms of fundamental units. An instrument based on the same principles as The Institute of Paper Chemistry instrument has been developed by the Kimberly Clark Corp. and was discussed recently in a paper by Roehr (*16*).

This treatment of this subject is obviously very superficial. An attempt, however feeble, has been made to cover the subject from a more fundamental point of view than is to be met with in the available published literature. We are aware that we have left a number of points dangling rather precariously. Nevertheless, if this stimulates further inquiry into this subject, this effort will have served its purpose.

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# Paperboard for Coating at High Solids

JOSEPH T. LOOMER

THE machine coating of paperboard today is still new enough in the industry to excite comment. Someday machine-coated board will be the rule rather than the exception and at these technical coating meetings there will probably be a subdivision just for board coating. To us in the board industry now engaged in machine coating it is obvious that the coating techniques and coating formulas must, of necessity, be different than those used in the machine coating of paper. But, by the same token, if the paper industry and their suppliers hadn't machine coat paper there probably would be no machine-coated board today.

It is the purpose of this paper to discuss the machine coating of paperboard, some of its problems, and in one instance describe a method now in use whereby the inherent qualities of paperboard and its method of manufacture finishes up with a coating technique substantially different from that used on paper.

Gair operates two high solids, roll-type machine coaters. For our purposes, high solids coaters employ coating formulations in excess of 50% solids. A Consolidated coater is used at our Piermont Division, and the entire process from beater room to printing and folding box is under direct control. An offset intaglio roll coater or Waldon Synchroset is used at the Tonawanda Division where the output of this machine is distributed as board to the trade. In this paper my remarks about machine-coated board will be confined to the Synchroset coater.

It isn't difficult to list the requirements for a good sheet of machine-coated board. They might be as follows:

1. A uniform surface as to brightness, smoothness, and color.
2. The coating should be waterproof, not only for offset printing, but for the odd converter that might use a coated sheet for a box exposed to wet hands, rain, or a change in humidity conditions.
3. The final coated sheet should be a good bender where called for, but also cut cleanly on high-speed boxmaking machines.
4. The finished sheet should be free of dust, lint, trim waste or any material in or on the sheet that would cause trouble during the printing operations.
5. And to add to all the foregoing it must print by offset, letterpress, or gravure, as well as flat or gloss ink, and then finally be able to run on a high-speed gluing machine.

The listing of requirements is simple, but meeting the requirements poses quite a few headaches. Based on machine-coated paper experience the printing requirements listed above usually run to three different coating formulas, and board is usually run on a caliper basis irrespective of the end printing requirement. It would be a little difficult to attempt to run all the flat ink orders together, all the gloss ink orders together, and then all the offset orders together using three different coating formulas. A board mill superintendent usually does not care very much to change caliper too often, especially when the change might be more than 5 points. Furthermore, the use of three different coating formulas are unwieldy especially when a customor might want only 5 tons of board for gloss ink in the middle of a 50-ton order for flat ink. Quite obviously the only solution for a board mill is to develop one coated board that will fit all the above-listed requirements with one coating formula or coating technique.

The manufacture of machine-coated board starts with the waste paper dealer and his sources of supply. The usual starting point is in the beater room but the waste dealer is mentioned because from him the mill superintendent must obtain the large part of his raw materials. The ironclad rule to be applied to raw materials used in machine-coated board in that if it isn't clean, leave it out. At the present time with the grades of waste available, this is pretty difficult to do. Although Gair has made intensive studies on cleaning systems for waste paper, expecially filler stock, the above rule still applies as there are no completely satisfactory cleaning systems available as yet. Some systems now in operation do a remarkable job, but faults in a cleaning system become all too obvious on lightweight machine-coated board. Pulp used, both bleached and unbleached, must also be top quality as regards color, cleanliness, and strength. Board furnishes for machine-coated raw stock must be clean and, in general, better than the furnishes for normal uncoated boards.

At this point the greatest single item necessary for a suitable raw stock for machine coating is the superintendent. His decisions, based on experience and raw materials available, will make or break a machine-coated board as far as meeting customer requirements. From the technical man's point of view we can check pulp as a raw material before it is used, but we can't tell too much about waste paper grades until they're pulped and then it may be too late. So at this point the immediate load is on the superintendent with whatever technical help he can be given.

The main furnish requirements are that it be clean, and when formed on the board machine, that it bend. From the beater room over the machine to the breaker calender stack these operations are standard board mill practice. Any detailed discussion of actual furnishes, beater room tackle employed or machine adjustments as to vat suction, flows, and press loadings have purposely been avoided. Too many different mills and superintendents have their own methods as to furnishes, treatment, and formation on the machine, and irrespective of how a raw stock is prepared for machine coating, if it has the following characteristics it will be suitable.

At the point where the sheet enters the first breaker calender stack, it must be clean, not only in the top liner, but in the sub and fillers to avoid grit, dirt, or any nonfibrous materials punching through. It must be close to caliper and weight and above all there must be a minimum of felt and wire marks in the top liner. Added to these requirements the base sheet must bend for although we have attempted to put the bender in the coating it still cannot replace the bender incorporated in the sheet in the beater room. The striving for a good bender must be tempered somewhat as the so-called sheet that "bends like a rubber boot" doesn't adapt itself very readily to the high-speed cutting action of some of the cutting and creasing dies now in use. One other point—what about size in the top liner? Size or lack of size doesn't appear to make too much difference as far as the coating operation is concerned. This is a matter for the judgment of the individual superintendent as to how he likes to form his top liner and his experiences with and without size on the curl of the finished board.

In effect to sum up some of the foregoing statements, the raw stock that we use for our machine-coated board is, of necessity, better than our best white patent coated grade.

The obvious question at this point is why use such a high-grade raw stock? If you have a machine coater supposedly you can take a low-colored, specky raw stock, and the coating will cover it up and make a beautiful white sheet irrespective of the color or dirt in the top liner. This can be done, of course, but the catch is to put on enough coating to accomplish

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the hiding of the raw stock. Speaking now of the roll coaters using high solids coating formulations the production limit for coat weight applied to board is about 3 pounds per thousand square feet. Experimentally, we have put on 5 to 6 pounds of coating per thousand square feet and if we could do this consistently the color and dirt in the raw stock would be covered up very nicely.

The drawbacks to these high coat weights lie in our lack of knowledge of coating formulations and in an inherent defect of the roll coaters which at heavy coating weights leave a definite coating pattern on the surface of the sheet. We can put on heavy coatings but in the case of the 6 pounds of coating described previously we had a discontinuous surface that would drive a printer crazy. On paper these heavy coating weights can be obtained as the supercalenders usually iron out this coating pattern. A 60-pound calendered one side paper sheet with 18 pounds of coating paper basis is 30% coating. A 20-point board sheet with 6 pounds of coating board basis has only about 7% coating weight. The cushion supplied by the board raw stock precludes the elimination of this coating pattern by supercalenders. Supercalendering coated board will reduce the pattern, but we don't have any supercalenders and the machine calenders are all that can be used. We must stay away from heavy coating weights until we can develop a coating technique to eliminate the coating pattern or add another coater to get our 6 pounds of coating in two steps of 3 pounds each.

Therefore, for the present, being limited to the application of coat weights between 1 to 3 pounds per thousand square feet, the raw stock has to be good because the coating application will make bad formation, dirt, felt, wire, and punch marks in the base sheet stick out like a sore thumb.

So much for the raw stock requirements. At this point the raw stock with all the aforementioned attributes is now leaving the last drier and entering the first breaker stack calender. We can now digress for a moment and look into the coating formulations as dictated by the end use of the finished coated board.

The finished coating must print letterpress, offset, and gravure. In effect the coating should be waterproof for offset and possibly also for letterpress and gravure where such boxes might be exposed to wet hands as in a soap carton. It must be ink receptive enough to print flat ink and ink resistant enough to print gloss ink.

As a starting point we arbitrarily chose casein as the coating adhesive because in our experience it waterproofed quite easily under certain conditions. This took care of one possible requirement but even with casein as an adhesive two formulas were required to adequately print flat and gloss ink. However, in the board industry, if handled correctly, the only difference on uncoated board suitable for flat or gloss ink printing was the strength of the starch solutions applied at the calender water boxes. If we could employ the advantages of the use of these water boxes one coating formulation would fit our needs. But before this could be done the coating must be completely waterproof on the machine in a distance of 60 feet with a board machine speed of perhaps 240 f.p.m.

The preparation of the coating color follows standard practice. Casein, cut with borax and made up of 17% solids is cooked in a steam-jacketed tank. The required amount of casein for a given batch is delivered to a sigma-bladed Day mixer, with the pigments, dispersing agents, dyes, and defoamers pugged directly in the casein solution. Water addition to the mix is made on a viscosity basis using a Brookfield variable speed viscosimeter for control. The completed coating batch is screened to the storage tank through a Cuno Auto Kleen filter.

The offset intaglio coater consists of a coating pan in which a rubber coating pick-up roll is rotated. This coating is squeezed into the cups of the intaglio roll, the excess doctored off the intaglio roll and returned to the coating pan. The coating is transferred to a soft rubber roll and then onto the sheet. A cast-iron backing roll to hold the sheet against the rubber roll completes the coater. For a more detailed description refer to Haywood's paper (*1*) on the offset intaglio coater in the 1948 *Tech. Assoc. Papers* or to the John Waldron Co. (*2*).

On the board machine, the coating section starts directly after the breaker stack calenders. The sheet leaves the breaker stack, passes up through the coater over two driers with a hot air blast against the top of the sheet, and finally over one additional drier and then into two finishing calenders. Prior to the development of our present coating techniques it was customary to run steam showers against the coated side of the sheet at the finishing calenders.

Considerable experimental work and machine trials went into the development of our present coating methods. There is apparently no easy way to get into machine coating and we made more than our share of broke. Ultimately we managed to get all the variables falling into place at the same time and our present coating technique is as follows:

By means of the water box at the breaker stack calenders we apply to the top side of the sheet a solution of glyoxal (*3*) in water or glyoxal in starch. While still moist the sheet then passes through the coater where the protein adhesive coating color is applied. The subsequent drying insolubilizes the coating by the time the sheet is ready to enter the first finishing calender. At this point, by means of a water box we can apply water or surface sizing materials to achieve a smoother coated surface and one easily adapted to print flat or gloss ink.

The advantages of the above method are obvious:

1. The addition of the insolubilizing agent prior to the coating poses none of the viscosity problems of addition of the insolubilizing agent to the coating.
2. Low amounts of adhesive can be used in the coating color as the function of the adhesive in this process is to hold the pigment in a waterproof state on the sheet. This low adhesive requirement results in a high pigment application per pound of coating applied, also higher brightness.
3. The starch or other surface sizing materials applied before or after the coating control the wax pick and the printing requirements.
4. The use of a water box applied after the coating gives a definite reduction in coating pattern thus enabling higher coating weights to be applied at the coater.

This process (*4*), of course, is possibly one of many that will be used in the machine coating of board. It is to some extent a direct departure from certain practices used in the machine coating of paper and possibly at this stage is peculiar only to board.

It is believed, however, as more and more companies enter into the machine-coated board field that a discussion of machine-coated board will not be confined only to the coating color, coater, and raw stock, but will embrace the possible calender treatments which, at the present time, control the printing requirements. Someday the Coating Committee of TAPPI will have to have separate discussions of machine-coated board due to the differences in approach that will arise in the coating of paper and coating of board.

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# Raw Stock for Machine-Coated Book Papers


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In discussing raw stock for machine-coated book papers, it is well to review the general properties and require-


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ments of these papers, whether produced on or off the machine. Once aware of these properties and requirements, it seems logical to discuss the raw stock as it affects these qualities.

The purpose of this paper is not to provide an absolute guide to be followed in the manufacture of coating raw stock, but rather to stimulate interest and careful thinking about those properties which have the greatest bearing on the physical characteristics, performance, and appearance of the finished sheet. In so doing, it is hoped that the many related problems may more readily be solved.

It is believed that a large portion of all book papers produced will be printed by the offset and wet-letterpress processes. Since these processes exert the greatest demand on coated papers, it follows that the manufacture of raw stock for this type of book paper presents the greatest problems. Of primary consideration is the internal strength of the raw stock which must be sufficient to prevent splitting and rupturing during the printing process. Along similar lines, the raw stock must be such that a good bond will be effected between coating and paper to prevent coating pick and subsequent dusting or smudging of the plates or blankets. The above-mentioned failures are generally the most common cause of complaint. Other strength characteristics such as fold, tear, and bursting strength must be maintained at high levels to withstand the abuse of modern high-speed commercial folders and automatic press feeders. Other properties of the raw stock which warrant much attention are those affecting brightness, smoothness and finish, dimensional stability, and cleanliness. All of these properties must be at higher levels than those at present for machine-coated publication papers. Table I illustrates this by listing the approximate standards for brightness, smoothness, and gloss as generally accepted by the merchant trade for nos. 1, 2, and 3 enamel papers. Approximate fold and tear standards are also listed (*1*). Again the values given are not definitely established standards, but do find general acceptance today.

The general discussion will consist mainly of three parts: (1) characteristics of the raw stock affecting surface strength, internal strength, and general strength characteristics of the coated sheet, (2) properties of the raw stock affecting brightness and color of the finished sheet, and (3) properties of raw stock affecting smoothness, dimensional stability, and cleanliness.

The manner in which a coating pick occurs and an hypothesis explaining why this type of pick occurs has been discussed by Singleterry (*2*) and Davidson (*3*). They concluded briefly that (1) a coating failure does not occur at the coating-paper interface, but rather in a certain zone a micron or so away from the interface within the coating, (2) the coating is actually "keyed" to the base stock, (3) coating pick occurs when the keys have been weakened through loss of adhesive solution from these keys, i.e., migration into the body stock.

On this basis the migration of adhesive into the body stock is a factor to be considered although it is felt that an effect of this type would be minimized somewhat by the high solids and high viscosity of the coating material used in machine coating.

A coating pick can be prevented in most cases by increasing the percentage of adhesive to a point where the strength of the keyed portion of coating always exceeds the internal strength of the raw stock. Doing this, however, generally has a deleterious effect on sheet properties such as brightness, gloss, and ink receptivity.

It behooves the papermaker, therefore, to impart properties in the raw stock that will prevent the migration of adhesive from the coating in order to obtain maximum coating strength with a minimum adhesive content. This appears to be in conflict with much of the data previously reported by Casey and Libby (*4*). That data, however, were obtained from sheets coated with a low solids coating at high coating weight where the penetration of adhesive was excessive. The maximum penetration of adhesive from coatings of high solids, however, is so small, comparatively, that much of these data may be invalid.

The manner in which this migration of adhesive is prevented depends upon the adhesive used. When a protein adhesive is employed a rosin-sized sheet may well be used since the alum present will cause precipitation of aluminum caseinate which will fill in the interfiber voids and reduce adhesive migration. This migration may also be reduced somewhat by the actual precipitation of protein as the pH of the solution at the interface is lowered to the isoelectric point by virtue of the raw stock acidity.

When starch is employed as the adhesive, an unsized sheet will allow intimate contact between the starch solution and the fiber walls with a resultant swelling of the fibers and subsequent reduction in adhesive migration. The utilization of a sized raw stock may be preferred. This sizing will contribute appreciably to other strength characteristics while preventing the penetration of adhesive. Rosin size has proved effective in this connection.

If the coating equipment is such that a size press is available for pretreating the raw stock a number of possibilities present themselves. Among these are: (1) the application of a pigmented wash coat to choke off the interfiber spaces, (2) application of a protein size, and (3) application of certain wet-strength resins (*5*).

The exact mechanism of the latter application is not fully understood though the possibility exists that the adhesive is adsorbed by the treated fibers and in this manner prevents adhesive migration. In addition to this, the incorporation of small percentages of wet-strength resin in the beater will result in better internal bonding.

The problem of splitting and rupture of the internal bond in the raw stock is far more serious and more difficult to control than coating pick. The pulps used and the manner in which the pulps are worked are the principal factors involved. The percentage of chemical pulp must necessarily be higher in raw stock for book papers than for publication papers. The actual percentage used and the *type* of chemical pulp used will be governed in most cases by economic conditions, the stock preparation system in the mill, and the availability of the chemical pulp, as well as groundwood, waste papers, etc. The incorporation of 15 to 20% of well-worked kraft will appreciably improve the resistance of a sheet to splitting. Much emphasis is placed on the preparation of the stock. Excessive percentages of chemical fiber are to no avail unless the maximum inherent strength of the fiber is obtained through good fibrillation while maintaining fiber length consistent with good formation.

It is impossible to establish even approximate standards for physical tests since these are dependent upon the furnish used, the degree of working, etc. It has been found that two physical tests having great significance as control devices, once standards have been established, are the wax pick and the bursting strength test. A drop in either of these tests alone does not necessarliy predict a tendency toward splitting, while a simultaneous drop in both tests is a danger signal. To illustrate this a specific case is cited. A 50-pound coating raw stock containing 40% virgin chemical fiber and 60% groundwood-free deinked fiber had the following minimum specifications:

| | |
|---|---|
| Bursting strength | 18 |
| Dennison wax | 8 |
| Density | 50 |
| Size (ink penetration) | 100 |

When the sheet was up to specifications, no splitting was encountered, except in the most severe cases of printing. Likewise, no correlation was observed between splitting and any of the following conditions: (1) a wax test as low as 6, (2) a burst test as low as 15, and (3) a low wax test *or* burst test coincident with low density and/or size test. When a

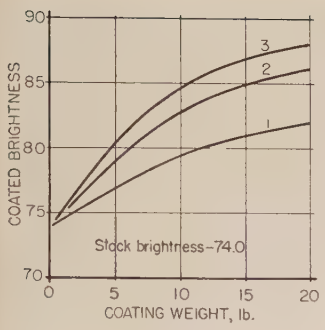


*Fig. 1*

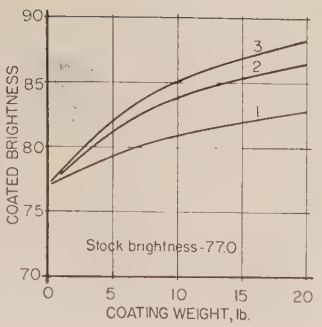


*Fig. 2*

drop in "wax" *and* burst were *both* observed, however, splitting almost invariably occurred.

The tendency of the above raw stock toward splitting was studied through the utilization of a printing pick tester that had been carefully correlated to actual press conditions. In addition, off machine-coated papers manufactured from this raw stock were studied on the pick tester and in the press-room with good correlation. It is expected that machine-coated papers would correlate even more closely since the excessive penetration of adhesive from the low solids coating in the case of off-machine papers would minimize the effects of low wax and low bursting strength.

Specifications and standards for these tests can best be determined through this, or similar procedures.

The attainment of brightness on a coated sheet is the function of raw stock brightness, coating weight applied, and pigmentation of the coating. A graphical representation of this is given in Figs. 1 and 2. Figure 1 is a plot of coating weight against coated sheet brightness with different pigmented coatings applied to a raw stock of 74 G.E. brightness. Figure 2 shows a similar plot on a raw stock of 77 G.E. brightness.

In any event, it is economically desirable to apply as heavy coating weight as possible. This is limited, of course, by the basis weight of the sheet, the equipment used, operating conditions, flow properties, and flexibility of the coating, etc. It may be seen from Figs. 1 and 2 that the raw stock brightness exerts its greatest influence on finished sheet brightness when a low coating weight is applied. The effect of highly pigmented coatings, however, is most noticeable at heavier coating weights.

Here again an economic balance must be established between the use of high brightness pulps in the raw stock and high brightness pigmentation of the coating. It may be desirable in some cases to utilize the extra strength of unbleached pulps while attaining brightness through coating pigments.

In other cases the use of high brightness pigments in the coating may lower the gloss of the finished sheet to such an extent that it becomes necessary to use bleached pulp entirely.

The smoothness of the coated sheet will be governed, to a large extent, by the coating operation and to a lesser extent by the finishing operation. The raw stock itself may greatly detract from surface smoothness, however. In general, the raw stock must be well formed to prevent mottling and a bumpy surface. Excessive moisture in the sheet prior to coating application will aggravate this condition by causing nonuniform penetration of the coating. The raw stock must be free of fuzz to prevent scratching and burring of the coating, in addition to causing over-all roughness. A pretreatment in the size press is of great value in this connection.

The moisture content of the raw stock must be sufficient to prevent cockling and subsequent stresses that will manifest themselves in the printing operation. Final moisture content, of course, must be controlled by the final drying operation.

The presence of shives and dirt specks must be kept at a minimum. It may be contended that the application of heavier coating weights of higher brightness will tend to cover these defects. Actually the higher brightness and finish of book papers simply present a greater contrast making them that much more objectionable.

In conclusion, it may be stated that in the manufacture of raw stock for coated book papers, the thinking with respect to strength, brightness, smoothness, and cleanliness is toward supremacy.

**Table I**[a]

| *Basis weight, lb.* | *G.E. brightness* | *B. & L. gloss* | *Bekk smoothness* | *Schopper fold*[b] | *Elmendorf tear*[b] |
|---|---|---|---|---|---|
| | | No. 1 enamel | | | |
| 70 | 80–85 | 60–72 | 1200–1600 | 30 | 45 |
| 80 | 80–85 | 60–72 | 1100–1400 | 30 | 55 |
| 100 | 80–85 | 60–72 | 1000–1300 | 30 | 75 |
| | | No. 2 enamel | | | |
| 70 | 77–81 | 50–60 | 1000–1300 | 20 | 40 |
| 80 | 77–81 | 50–60 | 900–1200 | 20 | 52 |
| 100 | 77–81 | 50–60 | 800–1100 | 20 | 70 |
| | | No. 3 enamel | | | |
| 70 | 75–78 | 45–55 | 950–1250 | 10 | 37 |
| 80 | 75–78 | 45–55 | 850–1150 | 10 | 45 |
| 100 | 75–78 | 45–55 | 750–950 | 10 | 63 |

[a] Tests at 50% relative humidity.
[b] Minimum either direction.


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# The Influence of Pulp Characteristics on Printing Papers


BRUCE H. WRIGHT


In the study of print quality many articles have been published on press and paper machine operation and on the characteristics and handling of printing inks, but the literature is practically devoid of material concerning the effect of the raw stock. This paper will therefore be confined to the characteristics of the individual pulps in printing paper furnishes and to their role in building a sheet suitable for further treatment in the manufacture and printing steps. The discussion will mostly concern coated magazine grades since they are prominent in the high quality printing field today. However, many of the statements will apply equally well to the manufacture of newsprint, rotogravure, and other grades printed on high-speed presses.

In the average run of printing papers no matter how much effort is put into improving the base sheet by coating or supercalendering, the quality of the *pulp* will be reflected in the finished print. If the pulp is suitable, the machine operator can form a sheet which will coat and super satisfactorily and which will afford the printer a good start on a successful printing run. However, if the pulp is of the wrong type, quality, or uniformity to begin with, no amount of doctoring by the papermaker, printer, or ink maker can develop a high-grade print.

In setting up qualifications for the fiber components in


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printing paper, it is well to first outline the characteristics in the finished sheet which are affected by the pulp. The most important of these are as follows: (1) uniformity, (2) smoothness, (3) compressibility, (4) resilience, (5) opacity, (6) over-all strength, (7) pick resistance, and (8) ink receptivity and absorption.

Such others as brightness, color permanence, gloss, wet rub, dirt, and sizing, while also important, are more applicable to specific grades of printing paper, and discussion of them would lead away from the general nature of this article.

## UNIFORMITY

Of the factors listed above, perhaps uniformity is of greater consequence to the printer than any other single factor. In setting up a print job, he must anticipate some variation in all his raw materials and tools. Neither his paper nor his ink can be identical from one run to another or even throughout a single run. Nor can he expect his plates to be perfectly dimensioned. He does have an effective means of compensating for minor variations in the thickness of his printing plates by raising low spots in the plate with paper shims, or backing. This procedure, called "makeready," is a very exacting process and may take several hours or even several days depending on the condition of the plates and importance of the job. Also, he has some control over his inks by thinning or thickening them. He can allow for some variation in paper thickness by increasing his printing pressure. However, if after he has taken all these pains to "match" his plate and ink to his paper there is any appreciable change in the paper, he may have to stop his presses in order to change his backing or his ink formula so that he can produce satisfactory prints. In either case there is a loss of time and money involved which can usually be prevented if the paper is uniform.

Just as nonuniformity of paper spells grief for the printer, nonuniformity of pulp means trouble for the papermaker. The latter can also absorb some variations, but when there are wide swings in pulp strength, freeness, fiber length, consistency, or furnish proportions the machine operator cannot be expected to produce uniform paper for the printer.

The means of obtaining pulp uniformity is really a subject all in itself but suffice it to say that frequent testing and proper standards along with good equipment and instrumentation will minimize the undesirable variations.

## SMOOTHNESS

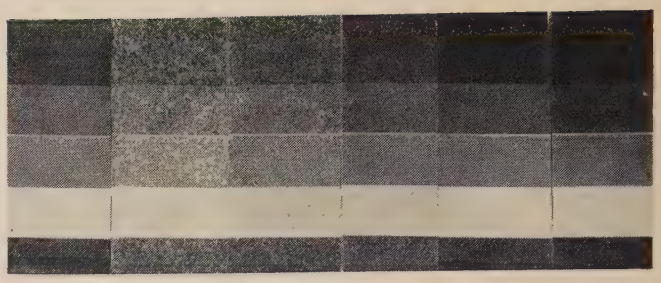
In the opinion of many investigators, smoothness of the sheet comes second only to uniformity in its effect on the quality of the print. The surface which the paper presents to the printing plate must be smooth for if it is full of hills and valleys there will certainly be points of no contact between paper and plate. Wherever such a point exists, the paper will not trap ink and the impression will not be true.

As pointed out previously, the printer may use heavier printing pressures in order to increase the contact area, but if the paper is too uneven, no amount of pressure will compensate for it. Furthermore, increased pressure tends to blur the impression by squeezing out ink on the high spots.

Paper smoothness can be traced directly back to the pulp in most grades since coating and supercalendering do not sufficiently "mask" the irregularities in the base sheet caused by the pulp.

There are two major factors contributing to base sheet smoothness, continuity of surface and formation of which the former will be taken up first.

In formulating a furnish which will have good surface continuity, it appears best to use the shortest, slimmest fibers available within the limits of strength requirements. Figures 1 and 2 explain this statement. They are photographs of softwood groundwood and sulphite pulp fractions made into TAPPI standard handsheets cut into strips, passed once



Whole pulp + 20 + 35 + 65 + 150 −150

*Fig. 1. Print tests groundwood fractions*

through the bottom nip of a mill supercalender, and printed together on a Vandercook proof press. The printing plate contains solid black areas at top and bottom and a gradation of half-tone dots in the three center strips.

It can be seen that the print appearance of both pulps improves markedly as the fiber length decreases. This results from the increased smoothness with shorter fiber length and is true of any pulp. The short fibers form a closer packed mass which lies flat, whereas the long fibers cannot be closely packed because of their extreme length and generally greater width resulting in a rough surface made up of holes and high spots.

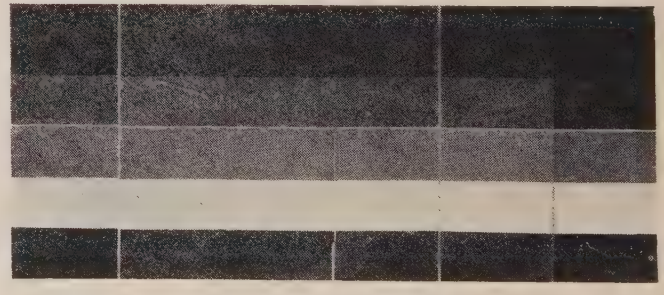
Purely from the standpoint of print appearance it might be said that a sheet for print grades should be furnished from 100% fines. Obviously this is not practical for several reasons, namely: (1) too low tearing strength, (2) increased wire mark which muddies the print, and (3) no practical means of producing such a pulp.

The influence of fiber width on print quality can be seen by comparing Fig. 2 with Fig. 3 (photograph of printed hardwood sulphite fractions). The average fiber width for the Fig. 3 pulp is over 20% less than that of the Fig. 2 pulp and it is apparent that every fraction has better printability than that of the Fig. 2 pulp.

It is apparent from Figs. 1 to 3 that the fractions of longer fibers print very poorly no matter what pulp is used. The +20 fractions are especially bad, and even the +35 fractions do not compare favorably with the finer ones. This is attributable to lack of surface continuity between the long fibers when formed into a sheet.

In groundwood, composed primarily of fines and other short fiber fractions, the effect of the long, poorer printing fractions is not too great if the amount of fiber in these fractions is kept at a minimum. However, in unrefined softwood sulphite composed for the most part of the long fractions, the effect of the long fibers is quite evident.

If the short-fibered groundwood is mixed in a furnish with the long-fibered sulphite in equal proportions, the printability of the mixture will be an improvement over that of the sulphite alone since the gaps will be partially filled with fine groundwood particles (see Fig. 4). However a close watch must be kept on the long fractions when using this mixture



Whole pulp + 20 + 35 + 65 + 150 − 150

*Fig. 2. Print tests bleached softwood sulphite fractions*

Whole pulp + 35 + 65 +150 − 150

*Fig. 3. Print tests bleached hardwood sulphite fractions*

in a print paper furnish since certain variations in sulphite preparation and in goundwood grinding and screening may increase the amount of the long fractions to a point where printability suffers.

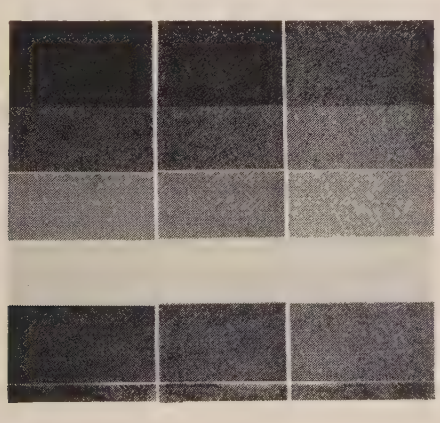
In addition to the effect of shorter fibers in forming a smoother, closer packed surface with smaller gaps between fibers, smoothness is influenced by formation. Any treatment of the pulp which increases the fibrillation will tend to make for clotty formation in the sheet. The sheet will then be composed of staggered thick spots where the fibers have clotted, interspersed with thin spots where there is practically a void of fibers. When poorly formed paper is supercalendered the thicker clots get more treatment and become hard. Then in the printing operation the hard spots tend to refuse the ink and mottly areas result. Furthermore, the existence of high hard spots prevents the plate from contacting the low spots resulting in even less ink reception and a generally poor print.

Much of the formation trouble may be eliminated by proper machine operation but only if the fibers are sufficiently short and unfibrillated since both these factors minimize clotting.

Although smoothness may be improved to a certain degree by supercalendering, it is more desirable to have it "built into the base sheet" so to speak, since excessive pressures on the supercalender tend to blacken the sheet and reduce the compressibility.

## COMPRESSIBILITY

There are differences in opinion as to what the term compressibility represents, but the following formula is suggested as being substantially correct as applied to pulp handsheets and paper when measured by the Time, Inc., Graphic Arts Laboratory Compressibility Tester:



100% groundwood | 50% groundwood 50% sulphite | 100% sulphite

*Fig. 4. Print tests comparison of pulps*

$$\text{Compressibility (\%) (at a given pressure)} = \frac{\text{Loss in caliper at a given pressure (in.)} \times 100}{\text{Original caliper (in.)}}$$

This instrument consists of a horizontal pressure foot $^1/_8$ by 1 inch which may be lowered vertically onto an anvil. Pressure may be applied on this foot by means of a regulating knob transmitting through a system of levers. A pressure-indicating gage is provided. Connected directly to the pressure foot is a caliper gage. In testing the compressibility of a sheet of paper or a pulp handsheet, the sheet is inserted between the foot and the anvil at zero pressure and its caliper obtained. Pressure is then raised to 1600 p.s.i. where it is maintained for 1 minute at which time the caliper is again obtained.

Theoretically, the more compressible a pulp or paper is, the more contact area that will exist between the printing plate and the printing medium, for the plate can force itself into the low spots which exist in any but a perfect medium. The printer often refers to this characteristic as "cushion." With a reasonably smooth sheet, this "cushion" gives him additional leeway in his makeready.

However with a very rough sheet, no amount of compressibility will counteract the poor impression caused by extreme hills and valleys in the sheet.

This can be illustrated by an explanation of the data in Table I.

**Table I. Compressibility of Groundwood and Bleached Softwood Sulphite Fractions at 1600 P.s.i.**

| | *Groundwood, %* | *Softwood sulphite, %* |
|---|---|---|
| Whole pulp | 49.4 | 33.5 |
| +20 | 64.2 | 35.2 |
| +35 | 63.2 | 35.1 |
| +65 | 60.2 | 33.4 |
| +150 | 54.3 | 32.6 |
| −150 | 43.7 | 29.7 |

In both pulps compressibility decreases as fiber length decreases. Yet Figs. 1 and 2 show that printability is improved as fiber length decreases. It is not reasonable to assume from this that printability improves as compressibility decreases and it is apparent that some other factor has obscured the effects of compressibility. The answer is undoubtedly smoothness.

The data also show that goundwood whole pulp is more compressible than sulphite whole pulp, agreeing with groundwood's printing superiority. It is probable that this advantage is derived from a combination of smoothness and compressibility.

Compressibility of pulp may be increased by softening the pulp with a caustic treatment during bleaching. The effect of caustic may also be observed in the high compressibility of bleached hardwood soda pulp. However, such treatment lowers strength and resiliency substantially and should be used with caution.

## RESILIENCY

Resiliency is closely akin to compressibility.

For the purposes of this paper, resiliency will be defined by the following formula:

$$\text{Resiliency (\%)} = \frac{\text{Caliper regained from 1600 p.s.i. after 1 minute} \times 100}{\text{Caliper lost at 1600 p.s.i.}}$$

It is obtained by carrying the compressibility test on to another step by releasing the pressure to zero quickly and again reading the caliper at the end of 1 minute in the relaxed condition.

Resiliency is not a particularly necessary characteristic in black-and-white printing but is quite important in four-color work. In this type of printing the paper is hit with four

separate plates bearing different colored ink. If the paper lacks resilience and does not "bounce back" to somewhere near its original caliper the printer may lose some of his leeway in makeready on the succeeding color plates. Then in order to make good contact he may have to increase pressures and run the risk of smearing the prints.

From the limited amount of experimentation with this variable, groundwood is known to have a fair degree of resiliency considering its high compressibility. On the other hand, the caustic treatment of sulphites in bleaching to improve compressibility seems to leave the pulp extremely low in resiliency. Most normally bleached chemical pulps seem to have a fair amount of it.

Much further work is necessary in determining the best means of measuring and controlling this characteristic.

## OPACITY

Opacity, or resistance to light penetration, plays a major part in papers which are printed on both sides of the sheet. Excellent prints are frequently spoiled in appearance by showthrough of the ink on the reverse side of the page.

Most of the adjustments of pulp characteristics which can be made to affect opacity are of a destructive nature. All bleaching processes lower opacity by removing the opaque coloring matters in the pulp. Beating and supercalendering also decreases opacity.

Of all the pulps available to the papermaker groundwood is by far the most opaque. By raising the groundwood content of the sheet it is possible to produce a more opaque paper, but if this measure is impractical it will then be necessary to fill the sheet with pigments or to increase the coat weight in order to obtain the increase in opacity.

## OVER-ALL STRENGTH

For operation on modern high-speed presses printing paper must possess a fair degree of strength. Weak paper means frequent press stoppages and lost time and money. The most vital strength needs are high tear and tensile to resist the stresses in operation on the presses. Dry tear is especially important in papers which are heat set after printing. Pick resistance, which will be treated separately, is necessary with most heavy inks.

The place to obtain the necessary strength is in the pulp itself but here is where the trouble arises. Nearly any steps taken to improve strength lower the printing quality. If long chemical fibers are included to enhance tearing strength print quality is lowered due to lower smoothness. If the chemical fibers are beaten to improve tensile, the increased fibrillation hinders formation and yields a mottly print.

It is best to add only enough long fibers to the furnish to obtain the necessary tear. To obtain the desired bursting and tensile strength, it is preferable to use measures which preserve the original pulp strength rather than to develop strength by fibrillating.

Usually some compromise between strength and print quality must be made. Here again wide variations in pulp uniformity should be avoided, in this case to maintain constant pulp strength.

## PICK RESISTANCE

Many fine prints are spoiled due to the lifting from the sheet surface of small chunks of paper or coating by the adhesive force of tacky inks at the instant the impression is made. This is known as picking and further affects the printing operation due to the deposition of these chunks on the printing plates where they transfer their impression to the succeeding prints.

The tendency for a coated paper to pick can be reduced by the use of thinner inks and by proper formulation of coating adhesive. However most picking failures can be traced to ruptures in the base sheet and can only be corrected by improving pulp strength.

Hardwood soda fibers are quite susceptible to picking and groundwood has caused some trouble. Again the fine balance between strength and printability comes into play in the decision as to what proportions of each component pulp are to be used in the furnish.

## INK ABSORPTION

In order to complete the picture of the influence of pulp characteristics and quality on printing a little attention should be given to ink absorption.

It has already been pointed out that hard spots caused by heavy supercalendering of formation clots inhibit absorption of ink on the surface of the paper.

Another problem arises when the ink is too highly absorbed into the interior of the sheet tending to gray the print and make it appear lifeless.

A further defect is caused when the oil vehicle is absorbed but does not carry the ink in with it. If the ink dries without sufficient vehicle it becomes chalky and tends to fall off.

The degree of oil absorption seems to be dependent upon the degree of openness of the surface. Thus a rough softwood sulphite sheet is more absorbent than a groundwood sheet which has good continuity of surface. If absorption is too great an increase in surface smoothness should help reduce it. However, it is possible to carry this too far in local areas as pointed out in the discussion of supercalendering above.

## SUMMARY

As with all other types of papers, there are no hard and fast rules for developing the furnish for a quality printing paper. It will depend on the actual use of the paper, the quality desired, the economic considerations, and the capabilities of the manufacturing equipment and personnel.

Whatever grade is being produced, special attention should be given to the uniformity of a pulp and to its ability to form a sheet with surface continuity and freedom from excessive formation clots. The best results are obtained by avoiding the use of extremely long wide fibers as much as possible and by maintaining an even distribution of long, intermediate, and fine fibers in order to close the sheet structure.

Compressibility, necessary for the cushioning effect in the presses, may be obtained with bulky pulps such as groundwood and soda. However, no amount of compressibility will help if the sheet surface is too rough.

Resiliency is needed for four-color printing. Groundwood is fairly high in this characteristic and most standard bleached chemical pulps have an adequate amount. However, drastically bleached pulps lose nearly all resiliency due to the softening treatment.

If additional opacity is needed to prevent showthrough, groundwood addition or increase is indicated. Bleaching, refining, and supercalendering tend to transparentize the pulp and lower opacity.

Pulp strength should be high enough to run on the machine and under strenuous conditions on high-speed presses. It must be able to resist the picking action of tacky inks. The sheet must also have sufficient strength to withstand the processing in the bindery as well as subsequent handling. In order to fulfill these requirements, some long strong fiber, such as softwood sulphite or kraft, must be used at the expense of printability.

Highly absorbent pulps tend to gray the prints and sometimes cause chalking. Ink absorption is reduced by closing the sheet and by supercalendering. However, it is possible to reduce ink absorption to such an extent by excessive supercalendering of high spots, that the surface will be nonreceptive and the print will be mottled.

It can be seen that pulp quality exerts considerable influence on the quality of the finished print. Therefore the printing paper manufacturer will do well to use his *pulps* to better advantage in obtaining good printing qualities rather than placing too much emphasis on subsequent operations.

# Instrumentation Studies. LXV. The K.B.B. Galvanic Size Tester

J. A. VAN DEN AKKER, and KEITH W. HARDACKER

**The K.B.B. galvanic size tester has been studied on the instrumentation program. Water is applied to the top surface of the test specimen by way of a sintered bronze electrode (porous); the specimen rests upon a zinc plate; this combination forms a galvanic cell whose internal resistance decreases as water transudes the specimen; the end point is taken when the current indicated by a microammeter connected across the two electrodes attains a certain value. The study includes observations on reproducibility, nonideal behavior of certain papers (such as buckling and cockling), probable influence of surface smoothness of specimen, discussion of the significance of the shape of current-time curves and of the crossing of such curves, evidence on the role played by water vapor, data on the influence of pinholes, study of the variation with time of the e.m.f. generated by the cell and of the probable influence of this variability on the accuracy of the end point, data on the influence of evaporative cooling of the reservoir, and a comparison of data obtained with the K.B.B., TAPPI, Currier, and fluorescence size testers. This report includes a listing of thirteen principal conclusions and a technical summary.**

In spite of the development over the years of literally dozens of size tests, there remains a need for a method which will reliably measure the resistance of paper to liquid water and which may be embodied in relatively simple equipment.

The dry indicator test (TAPPI Standard T 433 m-44) is generally recognized to be subject to grave personal error. It is not so generally known that the dry indicator test suffers a more deep-seated error in the case of papers whose size times are greater than about 30 seconds. It has been shown that, in the testing of hard-sized papers, the end point of this test is strongly influenced by water vapor, so that the apparent size time is a peculiar average result of the processes of transfer of water in the liquid and vapor phases (*1*). Indeed, in the case of very water-resistant papers, the end point is observed long before the completion of the transudation of the sheet by liquid water [as determined by the fluorescence size test and by other observations (*1*)]. Proponents of the dry indicator test advance the argument that it is immaterial how water passes through a sheet—that it is not a matter of concern how much of the transfer is by vapor and how much by liquid water—the water passes through the sheet, and the indicator signals that fact. This seemingly practical argument is in fact not practical, as is shown by the following considerations. First, in both technical and scientific work the greatest utility of measurement is obtained when variables are separated, as opposed to arbitrary combination imposed by the peculiar conditions of a test method. Second, the water-vapor permeability of hard-sized (but not impregnated) papers is high (*1*, *4*), so that the dry-indicator test provides only a crude measure of the water-vapor permeability of such papers, which in turn is not appreciably influenced by degree of sizing. Third, in consequence of the foregoing fact, the dry indicator test does not reliably distinguish between the degrees of sizing of hard-sized papers.

Thus, if the K.B.B. galvanic size tester provides a reliable measure of the resistance of paper to water, it would constitute a definite advance in the technology of the paper industry, for it has already been shown to be simple in both equipment and procedure and to be free of personal error (*2*). The present work was done with one instrument supplied for the duration of the study through the kindness of the manufacturer, Kelvin and Hughes, Ltd.,* of Glasgow, Scotland, and was planned with the hope that our observations together with those in the literature, might lead to an effective evaluation of the new method. The published data concerning the new method, leading to both pro and con opinions, are considerably richer than the information ordinarily given in support of, or against, a new method. The scheme of this report has been adjusted to this circumstance; the published findings and opinions of the earlier investigators will be actively incorporated with the data and discussions presented herein.

The method of the K.B.B. size tester was developed by Bridge, H. Ainsworth Harrison, and Wright, in cooperation with engineers of Kelvin and Hughes, and the former have published a description of the method and apparatus, together with observations and data relative to the performance of the new method (*2*). V. G. W. Harrison, Banks, and Poulter subjected the device to an instrumentation study, and concluded that the K.B.B. size tester does not provide "the improved method of testing so eagerly awaited" (*3*). Further data and discussion were then presented by Bridge and H. Ainsworth Harrison (*4*) in a rebuttal of the arguments set forth by V. G. W. Harrison, et al.†

## DESCRIPTION OF THE METHOD AND INSTRUMENT

A photograph of the instrument is given in Fig. 1. The terminals of a microammeter are connected directly to a pair of dissimilar metal electrodes. The lower electrode is of fairly pure zinc. The upper, moveable electrode is composed of "Porosint," a sintered bronze; it is sealed into the bottom of a metal housing and is nor-

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† Since the appearance of this report in its original form, our library has received a badly delayed copy of Proceedings of the Technical Section for 1948, containing further discussions of the evaluation of the K.B.B. size tester (*6*, *7*).

mally saturated with water. To perform a test, the operator places a specimen of paper upon the zinc electrode and lowers the Porosint electrode upon the paper, starting a stop watch at the instant of contact. The pair of dissimilar metals and the paper specimen form a galvanic cell; no other source of e.m.f. is present in the circuit. As the water (supplied by the saturated Porosint disk) penetrates into the paper, the resistance of the paper (i.e., the internal resistance of the galvanic cell) decreases, and the current indicated by the microammeter increases. In the normal use of the instrument, the watch is stopped when the current attains 80 microamperes and the time thus observed is taken as the size time.

At the conclusion of a test, the upper electrode is moved to a shallow dish containing a wetted pile of blotting paper disks and is placed upon the pile. The dish contains distilled water to a level just below the top of the pile of blotting paper. The dimensions of the voids in the Porosint disk are sufficiently small that capillary action maintains the disk in a completely soaked condition while the latter rests upon the wet blotting paper. However, the disk is not dripping wet when it is removed from the blotting paper to make a test. The total void volume of the sintered bronze disk is more than ample to supply water to heavy test specimens.

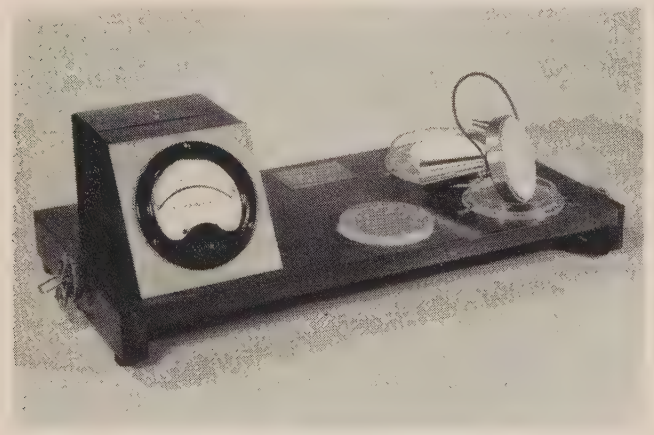


*Fig. 1. The K.B.B. galvanic size tester*

The metal housing to which the disk is sealed is furnished with a nipple, which is of aid in the initial filling of the Porosint (by suction) and, later, in backwashing the disk.

The microammeter is sufficiently rugged not to be damaged by an off-scale deflection if, inadvertently, the operator were to leave the upper electrode in place somewhat longer than is necessary. Because the viscosity and surface tension of water are functions of temperature, the results obtained with the new test (as with any size test) are temperature-dependent. Accordingly, care is exercised to maintain the temperature of the electrodes at a nearly constant value. Constancy of the relative humidity of the testing room is also important, so that the test is conducted in a constant-temperature, constant-relative humidity room. Also, the handle on the upper electrode is touched with the fingers for only the short time required to move the electrode.

## RESULTS AND DISCUSSION

A number of factors to be investigated will suggest themselves to persons familiar with the technical problems encountered in the evaluation of sizing. Most of these factors have been investigated or at least acknowledged by Bridge, H. Ainsworth Harrison, and Wright (*2*), V. G. W. Harrison, Banks, and Poulter (*3*), and by Bridge and H. Ainsworth Harrison (*4*). During our discussion of the data obtained by these people and by us, it will be necessary to make frequent reference to their publications. Because of the multiplicity and confusion of names, and because of the frequency of reference, we shall employ the abbreviations B-H-W (*2*), H-B-P (*3*), and B-H (*4*).

Our study involved 44 papers covering a variety of types and basis weights; these samples are listed in Table I. Prior to testing, all samples were conditioned in a testing room maintained at 73°F. and 50% R. H. Instead of simply measuring the 80-microampere endpoint time with the K.B.B. tester, the times were noted, for each specimen, when the current attained 10, 20, 30, 40, 60, 80, and 100 microamperes. This was done with the aid of time recordings on a kymograph, on which accurately known time intervals were also recorded. Five specimens from each sample were tested. The results are plotted in Figs. 2 to 5 for those specimens whose K.B.B. size times were greater than 20 seconds. The K.B.B. data for the 12 slack-sized samples are included in Table II, which presents all the data for the series obtained with the TAPPI, Currier, and fluorescence size tests.

In making the tests with the various instruments, care was exercised to ensure that the same side of the paper was wetted with water in each case. An unfortunate result of the magnitude of the work that had to be done and of the limited scheduling of work with the K.B.B. tester (imposed by customs regulations) was that the samples could not be tested with the four methods at the same time; there was an interval of a few months between the times of taking the data with the K.B.B. tester and the other three instruments. However, all but a few of the samples were of ages between a few months and several years, and the few less well-seasoned papers were in the laboratory for at least 2 or 3 weeks before testing, so that appreciable changes in sizing during the interim were not to be expected. An obvious improvement in the K.B.B. size tester was made at the onset of the work; the handle of the upper electrode was wrapped with cork sheeting to reduce the heat transfer from the hand to the electrode. (It seemed pointless to investigate the influence of warming by handling, because the substitution of a nonmetallic handle can be done so easily by the manufacturer or the user of the instrument.)

### *Personal Error and Reproducibility*

Requirements that are rudimentary but not, in themselves, sufficient for proper measurement are that the personal error should be small and the reproducibility good. The personal error is obviously small, because the operator has only to stop his watch at the instant the needle of the microammeter passes the 80-microampere mark; data given by B-H-W (*2*) illustrate the smallness of personal error and contrast this with the

**Table I. Papers Tested**

| Sample | Basis weight (25 × 40—500), lb. | Description |
|---|---|---|
| 1 | 53.5 | 25% rag, direct process |
| 2 | 47.0 | 50% rag, blueprint |
| 3 | 54.0 | 25% cotton, bond |
| 4 | 53.5 | 50% cotton, bond |
| 5 | 54.0 | 75% cotton, bond |
| 6 | 41.5 | 75% cotton, bond |
| 7 | 53.0 | 100% rag, bond |
| 8 | 77.0 | 100% rag, ledger |
| 9 | 54.0 | 50% rag, bond |
| 11 | 53.5 | White duplicator (sulphite) |
| 12 | 38.5 | White special form (sulphite) |
| 13 | 54.0 | White label (sulphite) |
| 14 | 90.5 | 100% rag, drawing |
| 15 | 56.0 | Hycar impregnated |
| 16 | 113.0 | Geon polyvinyl chloride resin impregnated |
| 17 | 26.5 | Untreated paper (see sample 18) |
| 18 | 26.5 | Sample 17 treated with melamine |
| 19 | 28.0 | Greaseproof; bleached and unbleached sulphite and broke; 4% urea-formaldehyde treated |
| 20 | 37.0 | 75–80% groundwood |
| 21 | 28.5 | Unwaxed breadwrap (see sample 38) |
| 22 | 46.5 | Coating raw stock |
| 23 | 50.0 | 100% bleached sulphite handsheets |
| 24 | 48.0 | 65% groundwood, 25% softwood unbleached sulphite, 10% softwood unbleached kraft; wallpaper stock |
| 25 | 90.0 | Jute liner |
| 26-A | 152.0 | Kraft liner, felt side |
| 26-B | | Kraft liner, wire side |
| 27 | 15.5 | Black kraft twisting |
| 28 | 22.0 | White manifold |
| 29 | 40.5 | White register, plain |
| 30 | 44.5 | Duplicator |
| 31 | 58.5 | Coating stock |
| 32 | 62.0 | Bag stock, slack sized |
| 33-A | 47.0 | Green, striped wrapper or bag stock; machine glazed side |
| 33-B | | Unglazed side |
| 34-A | 53.5 | Unbleached envelope stock; machine glazed side |
| 34-B | | Unglazed side |
| 35-A | 17.5 | Blue stock; machine glazed side |
| 35-B | | Unglazed side |
| 36 | 41.5 | Unbleached stock; wax emulsion treated |
| 37 | 113.5 | Red stock; dextrin treated; water finished |
| 38 | 41.0 | Waxed breadwrap; sample 21 waxed |
| 39-A | 85.0 | Unbleached stock; machine glazed side |
| 39-B | | Unglazed side |
| 40 | 120.5 | Asphalt-laminated building paper |
| 41 | 48.0 | 1.5% SPX sized, handsheets |
| 42 | 49.0 | 2.5% SPX sized, handsheets |
| 43 | 45.5 | 3.5% SPX sized, handsheets |
| 44 | 64.5 | SPX sized, machine run |
| 45 | 57.0 | 40% unbleached sulphite, 60% deinked; rosin sized; coating stock |

rather large personal error encountered in the use of the dry-indicator test. According to B-H-W (*2*), the reproducibility of the K.B.B. tester is good but this is refuted by H-B-P (*3*), who state that, according to their findings, "the potential developed by the galvanic cell is variable with time and erratic in behavior, and the observed current is directly dependent upon this potential—facts which militate against the use of the method for precision work." The former authors also showed that several instruments were in good agreement (*2*). Our data relative to reproducibility are presented in Table III, which gives the size times for the individual specimens (80-microampere end point). In each case, the first five values are the size times for the five specimens and the sixth value is the mean.

Inspection of the data given in Table III reveals that, in the great majority of cases, the deviations are about what one would expect on the basis of the variability of paper. The percentage differences between minimum and maximum values lie typically between roughly several per cent and 20%. There are a few rather large total variations—e.g., 30% for samples 30, 38, 39 (B side), and 42. There is little indication, however, that this variability is instrumental. There are a number of cases in which the total spread is only a few per cent—e.g., samples 6, 7, 8, 11, 26 (A side), 29, 31, 33 (A side), and 34 (A side). Unfortunately, five tests per sample are scarcely sufficient to enable a statistical analysis leading to a conclusion as to how much of the variability is attributable to the paper and how much is caused by erratic behavior of the instrument. On the basis of our data, we are inclined to agree with B-H-W (*2*) and B-H (*4*) in their conclusion that the K.B.B. tester is consistent.

**Table II. Size Times Obtained with the TAPPI, Currier Fluorescence, and K.B.B. Methods**

| Sample | Size times, sec. TAPPI | Currier | Fluorescence | K.B.B. |
|---|---|---|---|---|
| 1 | 40 | 20 | 51 | 48.7 |
| 2 | 32 | 18 | 44 | 46.0 |
| 3 | 40 | 27 | 55 | 55.4 |
| 4 | 38 | 19 | 50 | 57.5 |
| 5 | 40 | 24 | 51 | 57.2 |
| 6 | 26 | 13 | 30 | 31.5 |
| 7 | 31 | 21 | 40 | 52.2 |
| 8 | 56 | 39 | 89 | 86.2 |
| 9 | 37 | 24 | 58 | 58.9 |
| 11 | 43 | 28 | 66 | 61.1 |
| 12 | 28 | 16 | 40 | 31.3 |
| 13 | 44 | 27 | 68 | 64.4 |
| 14 | 73 | 56 | 130 | 204 |
| 15 | 68 | 17 | 80 | 123 |
| 16 | 20 | 9[a] | 9 | 13.8 |
| 17 | 15 | 4 | 15[b] | 13.6 |
| 18 | 19 | No sample | 14[b] | 13.9 |
| 19 | 19 | 4 | 17[b] | 11.3 |
| 20 | 20 | 6 | Below 7 sec. | 1.7 |
| 21 | 13 | Instantaneous | Below 7 sec. | 1.6 |
| 22 | 36 | 22 | 49 | 63.7 |
| 23 | 4 | 1 | Below 7 sec. | 1.6 |
| 24 | 41 | 32 | 92 | 101.9 |
| 25 | 3 | Instantaneous | Below 7 sec. | 1.1 |
| 26-A | 153 | 121 | Over 6 min. | 470 |
| 26-B | 101 | 72 | ..... | 189 |
| 27 | [c] | 1 | Below 7 sec. | 6.4 |
| 28 | 12 | 3 | 7[b] | 8.3 |
| 29 | 26 | 14 | 39 | 25.0 |
| 30 | 33 | 24 | 57 | 32.9 |
| 31 | 42 | 28 | 68 | 46.0 |
| 32 | 4 | 1 | Below 7 sec. | 2.2 |
| 33-A | 39[c] | 8 | 47 | 34.8 |
| 33-B | 43 | .... | 56 | 33.5 |
| 34-A | 40 | 21 | 73 | 62.1 |
| 34-B | 48 | .... | 73 | 57.7 |
| 35-A | 4[c] | Instantaneous | Below 7 sec. | 1.6 |
| 35-B | 3 | .... | Below 7 sec. | 0.6 |
| 36 | 53 | 58[a] | 89 | 78.3 |
| 37 | ...[c] | 136 | Over 6 min. | 345 |
| 38 (waxed bread wrap) | ... | 52 | Over 6 min. | 272 |
| 39-A | 84 | 56 | 176 | 166 |
| 39-B | 104 | .... | 185 | 141 |
| 40 (asphalt duplex) | ... | .... | ..... | ... |
| 41 | 37 | 26 | 52 | 61.4 |
| 42 | 36 | 30 | 66 | 89.4 |
| 43 | 39 | 35 | 78 | 99.2 |
| 44 | 100 | 72 | 268 | 214 |
| 45 | 29 | 15 | 39 | 46.7 |

[a] A grid consisting of single thickness of lens tissue was interposed between the lower plates and the specimen for the measurement. The grid was used only on those samples which appeared to be electrical conductors.
[b] The penetration of the water was observed to be "spotty."
[c] Sample was colored, making it difficult to determine the end point.

There is, however, the possibility that the method may enhance the error attributable to the variability of the paper; the adverse conclusion of H-B-P (*3*) regarding the reproducibility of the instrument might rest upon the chance that their paper samples were such as to result in this enhancement. Such enhancement could easily exist in view of our observation that certain samples—viz., samples 3, 4, 5 and 6—cockled on becoming wet, and sample 26 became saucer-shaped during the test. Since the electrodes are plane and rigid, this malformation of the paper would give rise to *increased* variation in the *apparent* size time, whereas this source of extra variability would be absent if the electrodes were perfectly flexible and made contact with the paper in all regions. Although this nonideal behavior of certain papers tested in the present study did not produce undue variability of the data, it is certainly conceivable that the effect could be quite appreciable. Even though the variability might be low, we feel that cockling, buckling, and dishing can produce an appreciable hidden error. This error is discussed in the following section.

***The Effect of Cockling, Buckling, and Dishing of the Paper***

Samples 3, 4, 5, and 6 produced audible snaps when cockles formed during the testing, and each snap was accompanied by a disturbance in the deflection of the microammeter needle. Obviously the cocklidg of these bond papers caused increase in the separation of the electrodes and diminution of the area of contact with the dry (lower) electrode—possibly also a diminution of the area in contact with the wet Porosint electrode. On becoming saucer-shaped during testing, sample 26 became concave on the felt side regardless of which side was in contact with the wetting electrode. This dishing caused the upper electrode (mass, 880 grams) to be raised about 1 mm. In a special run, a 5-pound weight was added to the upper electrode (total mass then 3150 grams), and the times to all currents were greatly reduced, even though the upper electrode was still raised by about 0.5 mm. In particular, the normal K.B.B. size time was reduced from 470 to 352 seconds. (It perhaps should be pointed out that the added mass increased the *platen* pressure, not the hydraulic pressure in the water, so that the decreased time is not attributable to an increased pressure gradient of water across the paper sheet.) It is evidently possible for this malformation of paper to cause an appreciable error in the K.B.B. reading.

Evidently this error would be negligible in the testing of a paper that lies flat when the end point is attained. It is concluded that we are here dealing with a source of error which depends upon the nature of the paper; in some, perhaps most, cases, this source of discrepancy would be negligible; in the testing of certain papers (particularly some heavy, strong, well-sized papers), the error could be quite serious. In our opinion, this source of error is probably the most serious of all to which the

**Table III. K.B.B. Size Times (Sec.) of the Individual Specimens (80-Microampere End Point)**

| *No. 1* | *No. 2* | *No. 3* | *No. 4* | *No. 5* | *No. 6* | *No. 7* | *No. 8* | *No. 9* | *No. 11* |
|---|---|---|---|---|---|---|---|---|---|
| 40.0 | 46.5 | 55.5 | 55.0 | 57.5 | 31.0 | 53.0 | 89.0 | .. | 60.5 |
| 49.0 | 47.0 | 51.5 | 53.5 | 56.0 | 31.0 | 54.0 | 85.0 | 54.5 | 61.0 |
| 52.5 | 42.0 | 56.5 | 57.5 | 67.5 | 32.0 | 50.0 | 85.5 | 58.0 | 60.5 |
| 51.5 | 50.0 | 55.0 | 55.0 | 54.0 | 32.0 | 51.5 | 89.0 | 60.5 | 62.5 |
| 50.5 | 44.5 | 58.5 | 66.5 | 51.0 | 31.5 | 52.5 | 82.5 | 62.5 | 61.0 |
| 48.7 | 46.0 | 55.4 | 57.5 | 57.2 | 31.5 | 52.2 | 86.2 | 58.9 | 61.1 |
| *No. 12* | *No. 13* | *No. 14* | *No. 15* | *No. 16* | *No. 17* | *No. 18* | *No. 19* | *No. 20* | *No. 21* |
| 32.0 | 55.5 | 178 | 114 | 14.5 | 12.5 | 14.5 | 11.5 | 2.0 | 1.8 |
| 29.0 | 61.5 | 202 | 116 | 13.5 | 14.0 | 13.5 | 11.0 | 1.6 | 1.8 |
| 30.5 | .. | 214 | 132 | 14.5 | 12.0 | 14.5 | 12.0 | 1.8 | 1.6 |
| 34.0 | 70.5 | 223 | 136 | 12.5 | 15.5 | 13.0 | 11.0 | 1.6 | 1.2 |
| 31.0 | 70.0 | 203 | 119 | 14.0 | 14.0 | 14.0 | 11.0 | 1.6 | 1.4 |
| 31.3 | 64.4 | 204 | 123 | 13.8 | 13.6 | 13.9 | 11.3 | 1.7 | 1.6 |
| *No. 22* | *No. 23* | *No. 24* | *No. 25* | *No. 26-A* | *No. 26-B* | *No. 27* | *No. 28* | *No. 29* | *No. 30* |
| 66.5 | 1.8 | 96.0 | 1.2 | 466 | 178 | 5.8 | 8.0 | 26.0 | 28.0 |
| 62.0 | 1.6 | 101.5 | 1.2 | 471 | 183 | 6.8 | 8.6 | 24.5 | 36.5 |
| 68.0 | 1.8 | 109.5 | 1.0 | 468 | 191 | 6.6 | 8.8 | 25.5 | 38.5 |
| 63.0 | 1.6 | 92.5 | 1.0 | 468 | 205 | 6.4 | 7.8 | 24.5 | 28.5 |
| 59.0 | 1.4 | 110.0 | 1.0 | 476 | 189 | 6.6 | 8.2 | 24.5 | 34.0 |
| 63.7 | 1.6 | 101.9 | 1.1 | 470 | 189 | 6.4 | 8.3 | 25.0 | 32.9 |
| *No. 31* | *No. 32* | *No. 33-A* | *No. 33-B* | *No. 34-A* | *No. 34-B* | *No. 35-A* | *No. 35-B* | *No. 36* | *No. 37* |
| 47.0 | 2.2 | 34.5 | 32.5 | 61.5 | 60.0 | 2.0 | 0.6 | 81.5 | 368 |
| 47.0 | 2.2 | 34.0 | 33.5 | 63.0 | 61.0 | 1.4 | 0.6 | 82.5 | 320 |
| 44.5 | 2.4 | 34.5 | 35.5 | 64.5 | 53.0 | 1.2 | 0.4 | 75.5 | 340 |
| 44.5 | 2.2 | 35.0 | 29.0 | 61.0 | 53.5 | 1.0 | 1.4 | 79.0 | 326 |
| 47.0 | 2.2 | 36.0 | 32.5 | 60.5 | 61.0 | 2.2 | 0.6 | 73.0 | 364 |
| 46.0 | 2.2 | 34.8 | 33.5 | 62.1 | 57.7 | 1.6 | 0.6 | 78.3 | 345 |
| *No. 38* | *No. 39-A* | *No. 39-B* | *No. 40* | *No. 41* | *No. 42* | *No. 43* | *No. 44* | *No. 45* | |
| 225 | 158 | 168 | Too water | 67.5 | 101.5 | 103.5 | 220 | 48.0 | |
| 310 | 166 | 124 | resistant | 59.0 | 89.5 | 94.5 | 210 | 49.0 | |
| 274 | 185 | 154 | | 60.5 | 87.5 | 106.0 | 228 | 48.0 | |
| 251 | 151 | 126 | | 59.0 | 74.5 | 84.0 | 212 | 45.0 | |
| 298 | 171 | 133 | | 61.0 | 94.0 | 108.0 | 201 | 43.5 | |
| 272 | 166 | 141 | | 61.4 | 89.4 | 99.2 | 214 | 46.7 | |

K.B.B. tester is subject. It is hoped that changes in the instrument design, intended to eliminate or minimize this error, will be found to be possible and successful.

### *The Effect of the Paper Surface*

The foregoing discussion naturally prompts a question concerning the influence on the K.B.B. size time of surface smoothness of the side of the paper in contact with the dry electrode. Most of the upper surface is wetted by water, so that the smoothness of the surface in contact with the Porosint electrode is not of so much consequence. Unhappily, the question cannot be answered by simply observing the influence on the data of testing papers that are rough on one side, and smooth on the other—first with the smooth side down and then with the rough side down—because we must assume that the water resistance and pore size of paper are not uniform throughout the thickness of the sheet. (One may not argue that the transudation time should be independent of which side of the paper is wetted on the basis that the water must pass all the way through the sheet, because this can be shown not to be true in the relatively very simple case of a capillary in which the radius and the angle of contact both vary along the length of the tube.)

However, by invoking the data obtained with the TAPPI and fluorescence size tests, we obtain some evidence regarding the influence on the K.B.B. data of the smoothness of the paper surface in contact with the zinc electrode. Samples 33, 34, 35, and 39 are glazed on one side, and are comparatively rough on the other side. In each case, side A is the smooth or glazed side. In the testing of the two sides of three of these four samples, a lower size time was observed when the glazed side was in contact with the zinc plate (side B in contact with the wetting electrode)(see Table II). According to the TAPPI and fluorescence size tests, these samples had a lower size time when the glazed side (side A) was in contact with the water; thus there seems to be little doubt that the transudation time should be less when side A is in contact with the water. When correction is made for the differences in size times for the two sides, we find that the K.B.B. tester would give a still greater difference between the two sides in the *wrong* direction. Relative to the result obtained for side A, the size time for side B (glazed side in contact with the lower, zinc plate) would be quite low. This is consistent with the rather self-evident notion that more general electrical contact can be made between the lower (dry) side of the paper and the zinc electrode when that side is smooth. Excepting smooth papers having good formation, it seems probable that this effect could account for an error of at least several per cent.

### *Choice of End Point*

There has been considerable discussion by B-H-W (*2*), H-B-P (*3*), and B-H (*4*) regarding the choice of the current to be taken as the end point of the test. The authors of the test (*2*) present electrical current versus time curves for a number of papers and show that, with the exception of a few anomalies, the curves do not seriously deviate from a common form; for example, the grading of the samples at 30 microamperes would be about the same as that based on an end-point current of 50 microamperes—excepting a few anomalous results. Part of the authors' argument is based on the linearity of the curves for currents in excess of about 20 microamperes, and on a comparison of the ratios of times for (a) 30 and 20 microamperes, and (b) 50 and 20 microamperes (*2*). V. G. W. Harrison, Banks, and Poulter (*3*) quite rightly criticize the contention that the curves are linear, pointing out that both the appearance of linearity and the region of apparent linearity depend upon the scale used in plotting, and they also discussed the insensitivity of the comparison of the ratios of currents. They permitted tests on papers to extend to relatively enormous currents, and showed that the curves crossed each other in regions other than the early region of small currents. They concluded that "*There is no way of telling from the form of the curves the moment when liquid water first touches the surface of the zinc plate on which the paper rests.* Under the recommended conditions of use it is doubtful whether *any* liquid water has completely penetrated the paper at the time of the arbitrary end point (except perhaps through pinholes). The gradings are certainly dependent to a marked extent upon the choice of end point and there seems to be no theoretical justification for choosing any one end point rather than another."

These observations are correct; they show that the K.B.B. size tester does not, and cannot, provide a *perfectly* accurate measure of size time. However, when one considers the probable mode of transfer of water through paper it seems very doubtful that anyone could create a rigorous definition of "size time" which would be acceptable to all competent and experienced technical men in the paper industry—let alone the task of devising an ideal size tester. It is naïve to think of the liquid water as advancing through the paper in a regular and uniform manner, with a plane front. Visual inspection of the fluorescence size test in a darkened place reveals strikingly the highly nonuniform manner with which water penetrates a sheet of (any) paper. Accordingly, even though the K.B.B. tester were ideal in all other respects, one would not expect the current versus time curve for paper to be of the form representable by a line at zero current running from zero time to the size time, at which time the curve becomes suddenly a vertical line rising to a finite current. In view of the nonuniform transfer of water, the current versus time curves *must* have a form similar to the published curves and to our curves presented in Figs. 2 to 5.

If we had an ideal method for recording the amount of liquid water which transudes a sheet as a function of time, we should obtain curves which start at zero at zero time, but start to rise slightly at small times (because of thin spots and imperfect spots), then rise with increasing slope, and finally round over to a horizontal line when all surface pores in the initially dry side of the sheet become filled with water to the point where capillary pressure is nearly atmospheric . The rising portion of the curves would have a shape resembling, in general form, that of the K.B.B. current versus time curves. More important, our recordings obtained with the hypothetical, ideal device *would cross over one another*. We would have a situation that might appear to be as hopeless as that of the K.B.B. curves in the eyes of H-B-P (*3*); in reality, the difficulty would be that of defining "size time"—a difficulty to which we have already re-

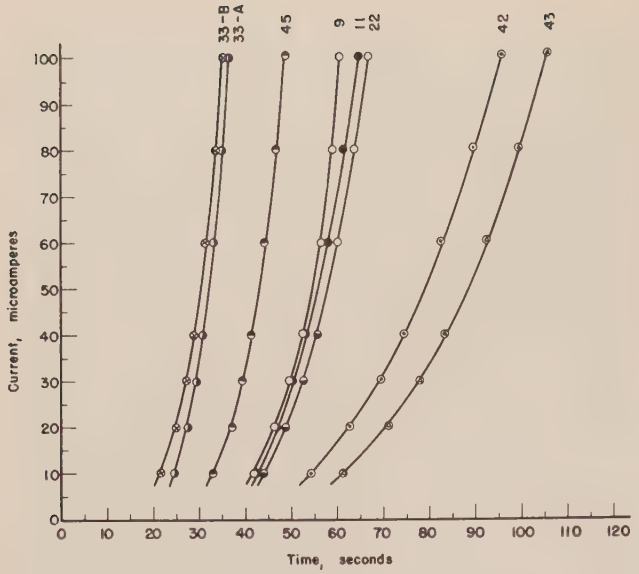



*Fig. 2. Current versus time curves for a portion of the samples; the normal end point is at 80 microamperes*

ferred. The curves obtained with the hypothetical device would cross each other because the forms for different papers would differ in degree; a curve for an extremely uniform paper would rise sharply in a short interval of time just below the size time, whereas that for an extremely nonuniform paper would rise gradually. Thus, the curves for many papers would present an array in which there would be a number of crossings.

It seems clear to us that the basic reasons for the crossings of the curves obtained with the K.B.B. size tester are those presented in the foregoing paragraph. However correct, or incorrect, the principle of operation of the K.B.B. tester, a current versus time curve for a very uniform paper should rise relatively sharply, whereas a gradual rise is to be expected in the case of a very nonuniform paper. Thus, with reference to Fig. 5, it is possible that sample 14 is more uniform than sample 44. (We are here referring to point-to-point uniformity rather than to specimen-to-specimen uniformity.)

Most of the curves presented in Figs. 2 to 5 are of similar shape. There is, of course, a little more crossing of curves than is evident at first inspection, because the curves have been distributed over four figures in the interest of reducing confusion. The obvious question to be raised when two curves cross (e.g., samples 14 and 44, Fig. 5) is: "Which sample has the greater size time?" On the basis of the 80-microampere end point, sample 44 has the greater size time but, if we adopted an end point at a current less than 60 microamperes, we would find that sample 14 had the greater size time. Again we feel compelled to say that we would meet the same problem if we had an ideal size tester. It becomes necessary to adopt an arbitrary end point—not just any point on the ascending portion of the ideal curve, of course—but some arbitrary point that is reasonable as, for example, a point midway between the beginning and the end of the transudation process, such midpoint being based not on time but on the amount of water attaining the initially dry side of the paper. If the end point for an actual test method is not too remote from the midpoint, the ranking of papers established by the test should not be essentially different from the ideal ranking—other sources of error in the method being negligible.

In rebutting the arguments of H-B-P (*3*) relative to the current versus time curves and the end point, the authors of the new test (*4*) justify their choice of 80 microamperes on the basis of "the need to prevent pinholes and weak spots from upsetting the measurement, the advisability of reducing the effect of differences in relative humidity, the desirability of maintaining only a low current flow in order to minimize polarization effects, and the practical advantage of keeping the testing time as low as possible consistent with other requirements." In further justification of this choice, the authors state: "With regard to lower currents, we showed in our first paper that crossings of the current/time curves in this range were definitely traceable to weak spots and pinholes in the paper; hence our reason for choosing some end point appreciably above the 20 to 30 microampere range." With regard to the further crossings observed by H-B-P (*3*) at quite high currents, the authors state: "In point of fact, from their own curves in Fig. 10 the first crossing of their current/time curves occurs at about 3.2 milliamperes, which we should regard as a very high current flow, being about 40 times greater than the recommended end point. What the significance of the numerous crossings of the curves at 5 to 8 milliamperes is we should not like to say definitely, but suggest that they are the result of the complicated time-dependent character of the cell, polarization, and back e.m.f. effects at these excessive currents. We do not think they have any concern with measurements made at the suggested end point of 80 microamperes." Thus, Bridge and H. Ainsworth Harrison (*4*) have arrived at their choice of end point on the basis of observation of operational factors. Actually, they have shown that the end point should not be less than about 80 microamperes, nor greater than about 3000 microamperes. There remains the excellent chance that a superior end point is to be found in the neighborhood of 1000 to 2000 microamperes, even though a choice of end point in this higher range would require a somewhat greater time of testing. This higher range is suggested because it might be nearer the hypothetical midpoint, discussed earlier. It is possible that a practical advantage would accrue from the use of a higher

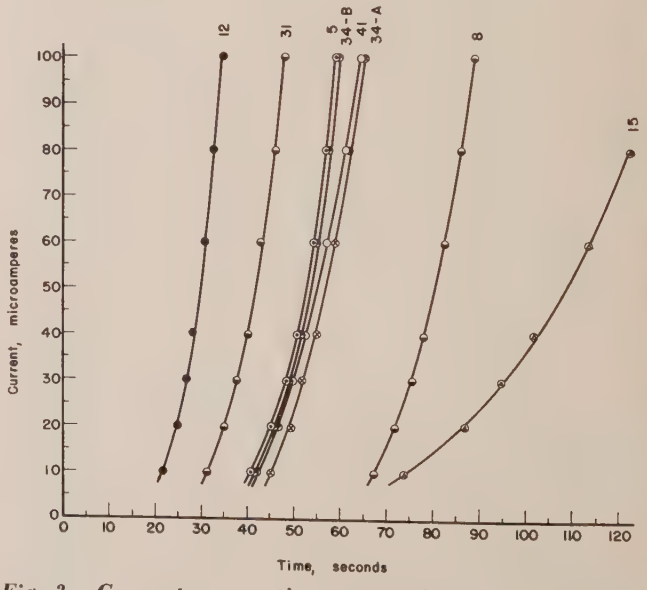



*Fig. 3. Current versus time curves for a portion of the samples; the normal end point is at 80 microamperes*

end point: papers which cockle, buckle, or dish on becoming wet would be more plastic at the higher average moisture content obtaining at the higher end point and, hence, might flatten out more under the weight of the upper electrode, and thereby reduce error arising in malformation (see the previous section on "The effect of cockling, buckling, and dishing of the paper").

### *A Criterion for a Penetration Test*

If paper were perfectly uniform and could be had in different thicknesses without modification of sheet structure, the penetration time ($t$) should be proportional to the square of the thickness ($d$). Actually, experimental work has shown that the equation $t = Kd^n$ fits experimental data quite well. In an application to the TAPPI and fluorescence size tests, using a special collection of papers made in different basis weights but with similar degree of sizing in each series, and using basis weight instead of thickness, it was found that $n = 1.4$ for the TAPPI test but that $n = 1.9$ for the fluorescence test (*1*). The substantial deviation from 2.00 observed with the TAPPI test is attributed to the strong dependence of that test on the transfer of water vapor.

Similar series of papers were not available for the present work. In spite of the obvious imperfections of testing two or more sheets simultaneously, it was felt to be of interest to obtain data on the influence of this kind of variation in thickness. Current versus time curves were obtained for one and two thicknesses of samples 8 and 12. The resulting curves, presented in Fig. 6, are interesting because (a) the times for two thicknesses are approximately four times the corresponding times for a single sheet (the theoretical factor for ideal conditions), and (b) if the K.B.B. size tester is primarily influenced by the transmission of water vapor, as claimed by H-B-P (*3*) (see the next section), one would expect the ratio of the times for double and single thicknesses to be less than four.

The normal K.B.B. size times were obtained for 1, 2, 4, and 8 thicknesses of sample 20, and for 1, 2, 4, and 5 thicknesses of sample 28. The observed size times are plotted against the number of thicknesses on log-log paper in Fig. 7. It will be seen that the data fit straight lines fairly nicely, showing that the empirical equation

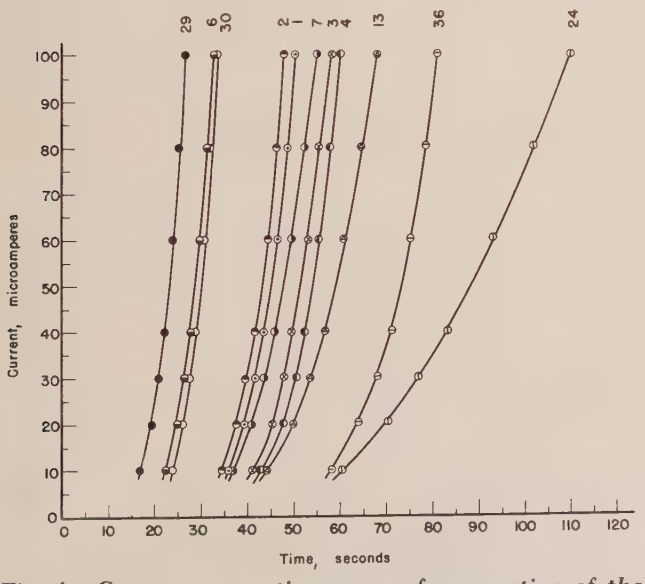



*Fig. 4. Current versus time curves for a portion of the samples; the normal end point is at 80 microamperes*

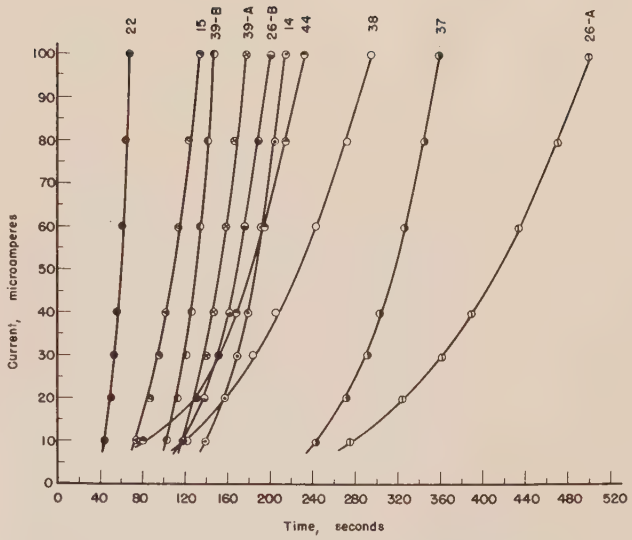



*Fig. 5. Current versus time curves for a portion of the samples; the normal end point is at 80 microamperes*

$t = kd^n$ is followed. The slopes of the lines are the values of $n$. These values are $n = 3.7$ for sample 20 and $n = 2.5$ for sample 28. If these values were substantially less than 2, we could be sure that the K.B.B. test is strongly subject to the water-vapor error. However, the values are greater than 2, which is possibly a consequence of imperfect transfer of water from one sheet to the next.

### *The Influence of Water Vapor*

Since it has been shown by H-B-P (*3*) that polarization effects and back e.m.f. are unimportant in the galvanic cell formed by the two electrodes and the specimen, the current indicated by the microammeter is simply $i = E/(g + R)$, where $E$ is the e.m.f. (slightly less than one volt and nearly constant), $g$ is the galvanometer resistance (constant), and R is the resistance of the paper between the electrodes. Having noted that the resistance of paper is a sharp function of the equilibrium relative humidity and that the size time is lessened by conditioning of the paper at increased relative humidity (a fact previously published by the authors of the test), H-B-P (*3*) conclude the following: "If the additional fact that the presence of salts in the damping water makes no appreciable difference to the numerical results of the test [B-H-W(*2*)] is taken into consideration, one can hardly avoid the conclusion that the changes in resistance $R$ (on which the whole test depends) are due more to the absorption of *vapor* by the fibers than to the filling of the capillaries between the fibers by liquid water. In other words, one is measuring something dependent more on the speed of advance of water vapor through the paper than the rate of liquid water penetration. *We believe this to be a fundamental drawback to the use of this and similar methods.*"

The foregoing conclusion by H-B-P (*3*), if justified, is naturally a serious criticism of the galvanic method. However, it has been effectively rebutted by B-H (*4*). After dismissing the possibility that the vapor *per se* could be responsible for conductivity (an irrelevancy), they state that "it is possible to suppose that the galvanic sizing tester is susceptible to the influence of moisture vapor in greater or lesser degree by virtue of its condensation as the liquid phase when adsorbed on

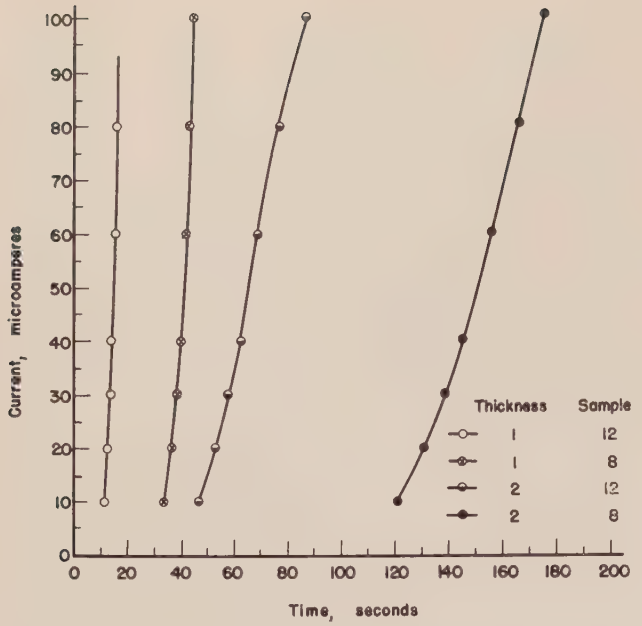



*Fig. 6. Current versus time curves for one and two thicknesses of paper tested simultaneously*

the cellulose fibers, in which case the electrical resistance of the paper will of course be reduced.

"Our first paper showed that almost invariably the sizing values obtained on the galvanic sizing tester are higher than those obtained by the dry indicator method. It is reasonable to assume that the mechanism of water/water vapor penetration in both these methods is of a similar nature. Therefore if 'one is measuring something dependent more on the speed of advance of water vapor through the paper than the rate of liquid water penetration,' it would appear that the dry indicator method is more susceptible still to the presence of water vapor!

"This is borne out by certain tests we have recently conducted. Several papers were tested on the galvanic sizing tester with a thin dusting of dry indicator on the bottom electrode. At 80 microamperes this indicator was not only changed in color but often was quite moist. Tests were then repeated in which the condition of the indicator was examined at lower current flow; these showed that the indicator was changing color uniformly at a current flow of 20 to 30 microamperes. To corroborate this, papers were tested by the normal dry indicator technique, and immediately the visual end point was reached they were rapidly transferred to the galvanic instrument and the top electrode put into position, when an initial current of 20 to 30 microamperes was recorded. This led us to conclude that if it is assumed that a water-vapor layer precedes the actual water front through the paper and that this water vapor layer interferes with technique for measuring sizing, then the galvanic sizing tester is less sensitive to its presence than is the dry indicator method and in this respect represents an improvement over the latter method."

The authors of the test then point out that, if water-vapor penetration (WVP) were an important factor, one should expect a correlation between the WVP of paper and its K.B.B. size time. In a series of three kraft laboratory sheets having WVP values of 753, 500, and 219 grams per sq. m. per day, the K.B.B. size times were, respectively, 83, 65, and 41 seconds. This constitutes a *negative* correlation where, if H-B-P (*3*) were correct, there should be a *positive* correlation. In a second experiment, bleached sulphite sized stock was treated with rosin/wax size emulsion to increase the water resistance; the WVP for the sheets made from these stocks were 414 and 461 grams per sq. m. per day and the K.B.B. size times were, respectively, 60.0 and 83.4 seconds—again, there was no correlation. In a third case, two commercial kraft papers were compared. These papers were alike in all respects except that one was engine sized and the other was unsized. The WVP's of the sized and unsized papers were 248 and 252 grams per sq. m. per day and the K.B.B. size times were 20 and 0 seconds. Another case cited involved extreme sizing—the times were so long, up to 3 hours, that water vapor should have brought about a near approach to an equilibrium condition long before the end points because the boards were pervious to water vapor. This case involved two vat-made lined chipboards having WVP's of 401 and 396 grams per sq. m. per day (virtually the same); the K.B.B. size times for these boards were 198 minutes and 51 minutes.

The data set forth by B-H (*4*) provide very convincing evidence that water vapor plays only a minor role in the K.B.B. test.

It seems probable that the lack of strong dependence of the K.B.B. test on water-vapor transfer is the result of the fact that the moisture content of cellulose, gained by adsorption from vapor at high relative humidity, is appreciably less than that of cellulose at a high relative humidity which had been wet with water to a moisture content somewhat in excess of the fiber saturation point (*5*). In short, it appears that there is a substantial difference between the electrical resistance of paper which has adsorbed moisture at a relative humidity just under 100% and the resistance of the paper which has a moisture content just above the fiber saturation point. A simple experiment corroborated the conclusion that the conductance of fibers moistened from the vapor phase only is insufficient to account for appreciable ef-

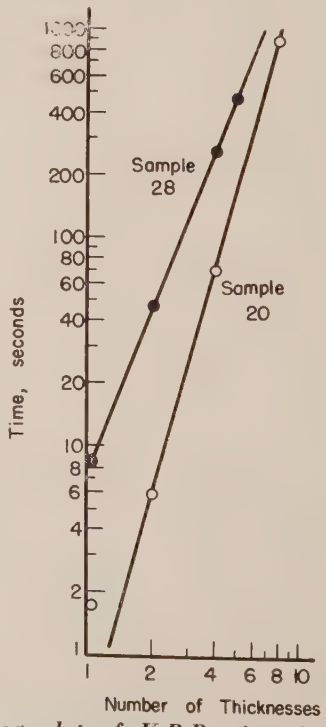



*Fig. 7. Log-log plot of K.B.B. size times versus the number of thicknesses of paper tested simultaneously*

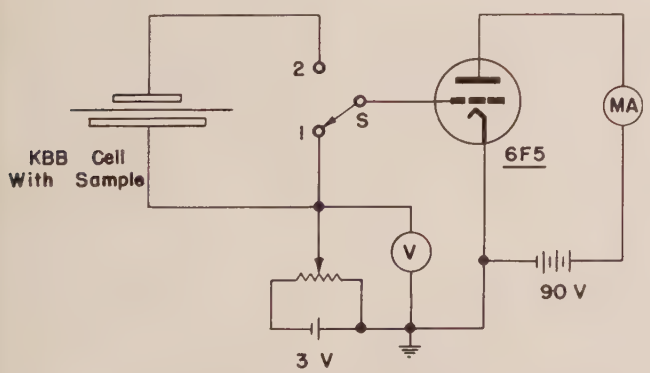
fect on the end-point current. A specimen of sample 24 (a paper which lies flat on wetting) was first conditioned over many hours at a relative humidity of 93%. It was then quickly inserted between the electrodes, the Porosint electrode being dry, and a current of 0.5 microampere was noted. (The meter was watched for 500 seconds and no further rise in current was observed.) To be sure, the relative humidity in the bottom layers of a specimen under test might rise to a value higher than 93% if the size time is very great (but it should be observed that layers above sorb moisture as the vapor penetrates the sheet). However, even on the assumption that it rises nearly to 100%, the conductance of the paper could scarcely be more than a factor of several times that of a specimen which had come to equilibrium at 93%, and the current resulting from the moisture sorbed from vapor would then be only a few microamperes, which would not cause appreciable error.

The evidence presented in the preceding section on "A criterion for a penetration test" further supports the conclusion that transfer of moisture by water vapor causes only a negligible error in a K.B.B. size time determination.

### *The Effect of Pinholes*

In view of the large error that can enter determinations with certain older electrical methods because of pinholes, one naturally asks how large are the errors in a K.B.B. determination resulting from such sheet imperfections. According to data presented by B-H-W(*2*), pinholes and deliberately produced perforations cause an error of only a few per cent at the 80-microampere end point. One of the principal reasons for the selection of 80 microamperes for the end point was that pinholes produce a rather substantial effect at small currents.

A number of experiments of specimens of samples 6 and 14 confirmed the findings of the authors of the new test. With the normal amount of water in the upper electrode system, the K.B.B. size times were found to fall within normal variations when pinholes of diameter 0.18 and 1.0 mm. were made in the specimens. When specimens having holes $^1/_8$ inch in diameter were tested, erratic results were obtained with sample 6 and surprisingly good results were had with sample 14. Obviously, no one would test specimens having such conspicuous imperfections. It perhaps should be mentioned that greater sensitivity to pinholes was observed




FLOATING GRID CIRCUIT

*Fig. 8. Vacuum tube voltmeter employing the floating grid principle, for measuring the e.m.f. generated in the galvanic cell*

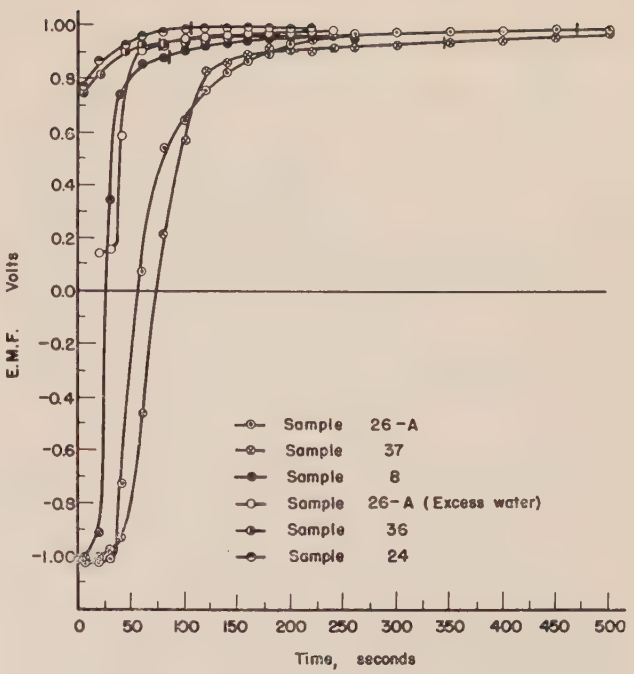



*Fig. 9. Variation with time of the generated e.m.f. Vertical dashes cutting the curves denote the end-point times (determined in separate runs)*

when the upper electrode system was deliberately furnished with an excess of water. In using the instrument in accordance with recommended procedure, the upper electrode system could not have an excess of water.

### *Variation of E.M.F. During a Test*

V. G. W. Harrison, Banks, and Poulter (*3*) properly point out that variability of the e.m.f. generated by the galvanic cell would result in variability of the apparent size time. Much of their work (accomplished with a vacuum tube voltmeter), however, was not relevant to the actual conditions of test. This is made clear by B-H (*4*), who state that the e.m.f. *at the moment of the end point* is the important thing. This, of course, cannot be denied. They measured the e.m.f. (open-circuit potential difference between the electrodes) with a vacuum tube voltmeter and found that, for 16 samples of paper, the e.m.f. varied between 0.960 and 0.998 volt, or about 2% from average, at the outside.

This consideration is an important one, which we felt it desirable to investigate. We employed the vacuum tube voltmeter shown in Fig. 8. The floating grid principle was used, so that the impedance of the electronic voltmeter was extremely high—undoubtedly many times that of the dry paper. With the switch isolated between points 1 and 2 (Fig. 8), the plate current was noted. Then the grid was connected to point 1 and the voltage was adjusted to return the plate current to the floating grid value; there was then no current flowing to the grid. On switching to point 2 and readjusting the voltage to obtain the floating grid plate current, the change in voltmeter reading was numerically equal to the e.m.f. to be measured.

The results obtained for several samples are given in Fig. 9. It is of considerable academic interest that some of the initial e.m.f.'s, for the dry dielectric, were negative relative to the final values. (This effect was not due to an initial charge on the upper electrode.)

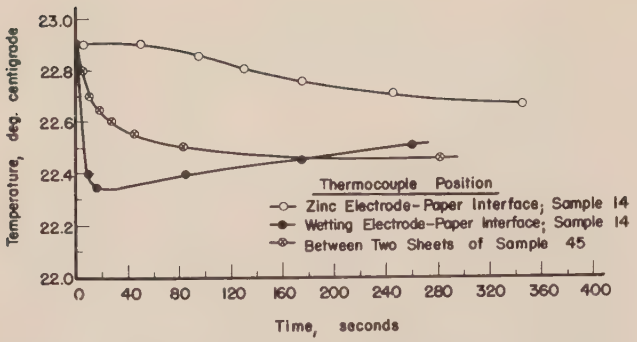



*Fig. 10. Variation with time of the temperature at three points between the electrodes*

The important result is the finding, in agreement with B-H (*4*), that the e.m.f's at the end points were not greatly different from one another. The end-point times are designated in Fig. 9 with short vertical dashes.

The lowest e.m.f. observed by us was about 0.888 volt (sample 8), and the highest about 0.98 volt (sample 24), a total spread of 10%. In the absence of further information, we must assume that this would result in a spread of 10% in the current. Because of the steepness of the current versus time curves, this variability in the e.m.f. is responsible for only a small change in the end-point time—for example, a total spread of about one second in a 60-second test. Earlier in this report (see the section on "Choice of end point") it was suggested that the end-point current might profitably be increased to a substantially higher value. A further advantage of a higher end-point current is suggested by the curves given in Fig. 9; it will be seen that the curves tend to converge to a smaller range with increasing time, thus indicating that a somewhat longer test result would involve a smaller variation in the end-point e.m.f.

### *The Effect of Temperature*

It is well known that a variation in temperature will influence the accuracy of any liquid penetration test. The authors of the test therefore investigated the influence of temperature, and prepared a chart showing the typical variation of K.B.B. size time with temperature. At room temperature, the variation is about 2.5 per cent per degree F. This is roughly twice the variation with temperature of the ratio of surface tension to viscosity of water. Of course, there are two other significant factors which cause the size time to decrease with temperature, and these probably account for the other half of the observed temperature dependence: the electrical resistance of the wetted test specimen decreases with increasing temperature, and the contact angle between the water and the fiber decreases, both of which factors hasten the end point. In view of their results, B-H-W (*2*) recommend that the temperature at which the test is conducted be carefully standardized and maintained within ±1°F.

The magnitude of the effect of evaporative cooling of the pile of wet blotting paper (which would occur most appreciably when the upper electrode has been removed to storage or test position) appeared to us to be a matter of potential importance. Various temperatures were measured under typical operating conditions by means of a fine copper-constantan thermocouple. At the time these measurements were made, the temperatures (in °C.) of the air and of various parts of the instrument were as follows:

| | |
|---|---|
| Air | 22.9 |
| Water in shallow dish | 21.7 |
| Wetting electrode housing | 22.4 |
| Zinc electrode | 22.9 |
| Interface between the Porosint and wetting pad | 22.3 |

The variation of temperature with time at three points during typical testing is shown in Fig. 10. Evidently the temperature variation is of the order of 0.5°C., or roughly 1°F. It should be recalled that we wrapped the handle on the upper electrode system with cork sheeting to minimize the heat transfer from the hand to the Porosint disk.

### *Correlation with Other Size Tests*

TAPPI, Currier, and fluorescence size times are plotted against the K.B.B. size times in Figs. 11, 12, and 13. As is usually the case in comparing size tests, one observes only a rough correlation. The correlation coefficient, if computed, would undoubtedly be fairly high; the magnitudes of correlation coefficients are usually misleading to persons unfamiliar with statistics. We are here more concerned with the inversions of ranking that can be encountered and the associated magnitudes. Numerous inversions will be seen in the three figures. If, at first glance, the correlation between the TAPPI size test and the K.B.B. tester appears to be good, attention is directed to two samples for which the TAPPI size times are about 42 seconds—the corresponding K.B.B. size times are 46 and 102 seconds. In one case, it will be noted that the TAPPI size time is 20 seconds, whereas that determined with the K.B.B. tester was only 1.7 seconds; this sample contains 75 to 80% groundwood, and the discrepancy is attributed to the self sizing of the groundwood that occurred between the tests. This high groundwood content sample should not have been included in this study.

Large inversions are also seen in the comparison of the Currier and K.B.B. data and also in the plot of fluorescence size times versus the K.B.B. results (Fig. 13). With regard to the latter, it is interesting to note that a curve of best fit would be a nearly straight line at 45° with the axes; that is, on the average, the fluorescence and K.B.B. size testers yield about the same numerical value. The magnitudes of the deviations away from a curve of best fit are rather large, however, frequently being of the order of 10 to 15 seconds. Where applicable (see below), the fluorescence size tester is believed to provide a fundamentally accurate measure of size time (*1*). However, its end point had arbitrarily been set at the smallest size time of three reasonable choices, and it is possible that this accounts

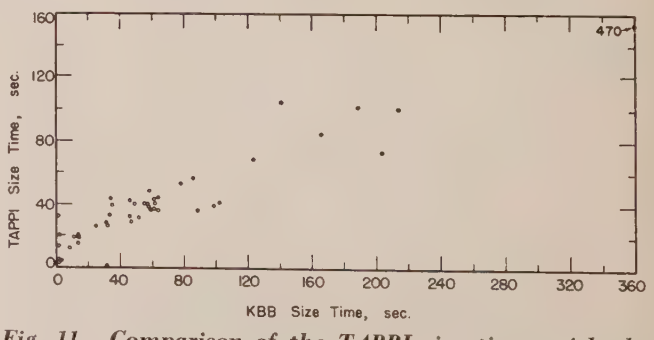



*Fig. 11. Comparison of the TAPPI size times with the K.B.B. size times*

for the imperfect correlation with the K.B.B. tester. Another probable cause of imperfect correlation is the error, in the testing of certain samples with the K.B.B. instrument, resulting from cockling, buckling, or dishing of the specimens. The source of error resulting from roughness of the side of the specimen in contact with the zinc electrode would probably contribute to the imperfect correlation. There are certain types of papers for which the fluorescence size tester does not function well. These are usually unbleached kraft papers and the failure of the test is caused by a quenching of the fluorescence.

***Miscellaneous Comments***

We are not ordinarily concerned in these studies with such aspects of an instrument as its appearance and convenience in use. We should like to refer, however, to the common sense employed in the design of the K.B.B. instrument; it is simple and modest, but attractive—there is no so-called "streamlining." The instrument is extremely simple to use.

The influence of small amounts of dissolved salts during test was simulated by B-H-W (*2*) in testing with distilled water, with water containing 1% aluminum sulphate, and with water containing 1% sodium chloride. The presence of the salts did not affect the size time.

The two electrodes should be maintained in a clean condition. The wetting electrode tends to accumulate impurities from frequent contact with paper specimens, and should be cleaned by backwashing. The wetting disks of blotting paper should, of course, be changed at reasonably frequent intervals.

Principal conclusions concerning the K.B.B. galvanic size tester:

1. The personal error is negligible.
2. Reproducibility of the instrument is good.
3. The instrument might be in appreciable error in the testing of papers which cockle, buckle, or become saucer-shaped on wetting. The error can be reduced by increasing the load on the upper electrode, and it seems likely that increasing the end-point current would also reduce the error by increasing the plasticity of the specimen.
4. It is probable that an appreciable error can arise when the surface of the paper in contact with the zinc electrode is not smooth.
5. The crossing of the current versus time curves (involved only in a study of the method) is to be expected as a consequence of variation from paper to paper of the *degree of uniformity* of paper, and such crossing is not indicative of nonideal behavior. Difficulty in selecting an arbitrary end point is basically a difficulty in defining size time when the probable nature of the transudation of water through paper is considered.
6. It is suggested that the end-point current be made greater than 80 microamperes. Such an increase would have the following advantages: (a) the present end point is probably below the midpoint of the transudation process, (b) a greater time of test would cause the specimen to be more plastic, and it is possible that error resulting from cockling, buckling, and dishing would be rendered smaller, and (c) a greater time of test would result in less variability of e.m.f. at the end point.
7. The K.B.B. size tester at least approximately satisfies the criterion for a penetration test that the transudation time should be proportional to the square of the number of sheets simultaneously tested.
8. Transfer of moisture through paper via the vapor phase has only negligible influence on the observed size time.
9. "Pinholes" in the paper cause only a small error.
10. The variation, from paper to paper, of the end-point e.m.f. in the circuit is somewhat larger than previously reported but, because of the steepness of the current versus time curve, the error introduced is less than about 1% (relative to average) of the observed size time.
11. Because of evaporative cooling, the temperature of the transuding water may be 0.5°C. different from that of the room. This temperature difference corresponds to an error of 2.5%, but the average error arising in this effect would probably be less than 1%.
12. The K.B.B. size times correlate roughly with those obtained with the TAPPI, Currier, and fluorescence size tests. However, in each case, inversions and individual deviations are quite large (see Figs. 11, 12, and 13).
13. The K.B.B. size tester is markedly superior to the TAPPI (dry indicator) size test. We believe that it is the best of the simple size testing methods, but probably not as accurate as the fluorescence size tester and, perhaps, other research methods. Certain improvements, relating to conclusions 3, 4, 6, and 11, should be investigated by the authors of the test (*2*) and effected if feasible.

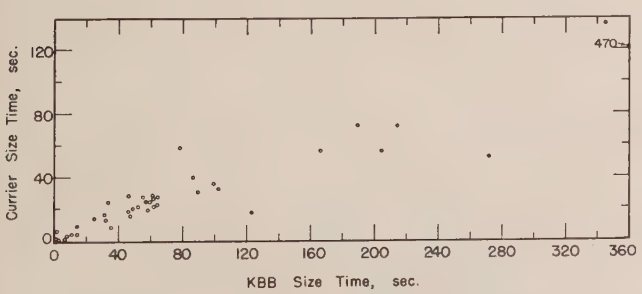



***Fig. 12. Comparison of the Currier size times with the K.B.B. size times***

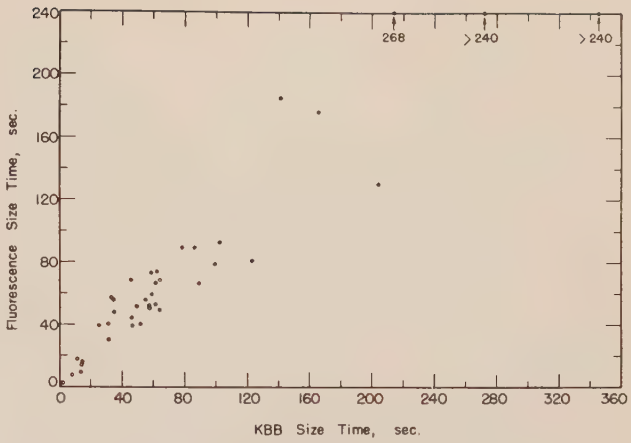



***Fig. 13. Comparison of the fluorescence size times with the K.B.B. size times***

## SUMMARY

There is a need for a reliable size tester involving

simple equipment. The existing standard method (TAPPI dry indicator test) suffers at least two serious shortcomings.

The K.B.B. tester consists simply of two electrodes of dissimilar metals (one composed of zinc and the other of porous bronze saturated with water) that are separated by the test specimen and connected to a microammeter. The method is free of personal error, and several instruments yield concurring data. However, the literature contains strongly conflicting opinions, which are included in the discussions presented in this report.

The end point of the normal test is attained when the current generated in the simple circuit reaches 80 microamperes; however, for research purposes, determinations are made for the plotting of current versus time curves. The reproducibility of the instrument is satisfactory, as judged by tests on five specimens of each of 44 samples of paper.

Certain papers cockle, buckle, or dish when wet and, in some instances, the stresses are sufficient to raise the upper, wetting electrode noticeably. Increasing the load on the upper electrode decreases the instrumental reading, and it is evident that such behavior of certain papers causes error. This error, where encountered, is probably the most serious of the several errors to which the K.B.B. tester is subject. Remedy is urged.

In similar vein, the character of the surface of the paper in contact with the lower (dry) electrode probably influences the test result, especially if that surface is not smooth and the formation is poor. Evidence is presented which indicates that this source of error is real and in some cases substantial.

The crossing of the current versus time curves for various papers has been taken by a PATRA group as an indication of nonideal behavior of the K.B.B. tester. Such crossing is to be expected even in an ideal size tester and is a consequence of the variation from paper to paper of the *degree of uniformity* of paper. Difficulty in arbitrarily selecting an end-point current is basically a difficulty in defining size time. The currently adopted end point of 80 microamperes was adopted by the authors of the test on the basis of operational factors.

Actually, they have shown that the end-point current should not be less than 80 microamperes, and that it should not be as large as several thousand microamperes It is suggested that the end point be increased, perhaps to some point between 1000 and 2000 microamperes, because the end point might then be closer to the midpoint of the transudation process. Other advantages resulting from an increase in the end-point current would be greater plasticity of the test specimen, possibly less error because of cockling and other malformations, and smaller variability of the end-point e.m.f.

The K.B.B. size tester at least qualitatively meets the criterion for any penetration test that the transudation time should be proportional to the square of the number of sheets simultaneously tested. (The simultaneous testing of more than one sheet is not a normal function of the instrument.)

A complete discussion of the influence on the test of the transfer of moisture through the paper via the vapor phase leads to the conclusion that such influence is only of a minor nature. The lack of strong dependence of the test on water vapor transfer is probably the result of the fact that the moisture content of cellulose, gained by adsorption from vapor at high relative humidity, is appreciably less than that of cellulose at high relative humidity which had been wet with water to a moisture content somewhat in excess of the fiber saturation point.

The smallness of the effect of pinholes in the paper has been corroborated. Pinholes seem to have an appreciable effect only when large or when an excess of water is deliberately placed in the wetting electrode system; such an excess cannot exist in the normal use of the instrument.

The variation, from paper to paper, of the end-point e.m.f. is somewhat larger than previously reported by the authors of the test but, because of the nature of the current versus time relation, the influence on test results of this variability is negligible.

Evaporative cooling of the water in the reservoir (from which the wetting electrode picks up water) causes temperatures at various points in the test to be somewhat lower than room temperature. Such temperatures were measured with a fine thermocouple, and the maximum differences in temperature from that of the room were of the order of 0.5°C. In actual practice, such temperature differences might remain fairly steady.

The K.B.B. size times are compared in the report with those determined with the TAPPI, Currier, and fluorescence size tests. Rough correlations are found; certain inversions are serious, and a number of deviations from perfect correlation are correspondingly large, in each comparison.

Thirteen principal conclusions are listed at the end of the report. The last of these is as follows: The K.B.B. size tester is markedly superior to the TAPPI (dry indicator) test. We believe that it is the best of simple size testing methods, but probably not as accurate as the fluorescence size tester and perhaps other research methods. Certain improvements, relating to conclusions 3, 4, 6, and 11, should be investigated by the authors of the test (*2*) and effected, if feasible.

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This report is one of a series issued as a part of the Instrumentation Program of the American Paper and Pulp Association. The data in this paper were reported to the Association as Report No. 44, dated Jan. 15, 1950.

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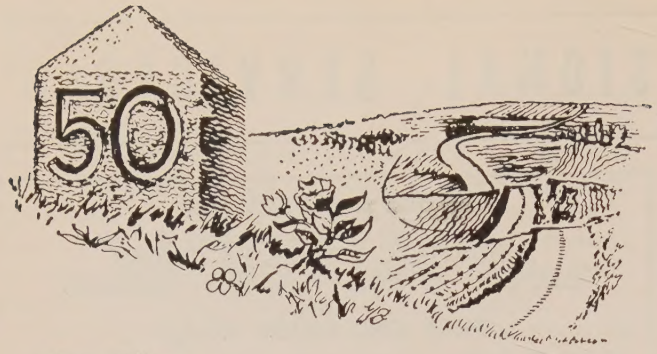

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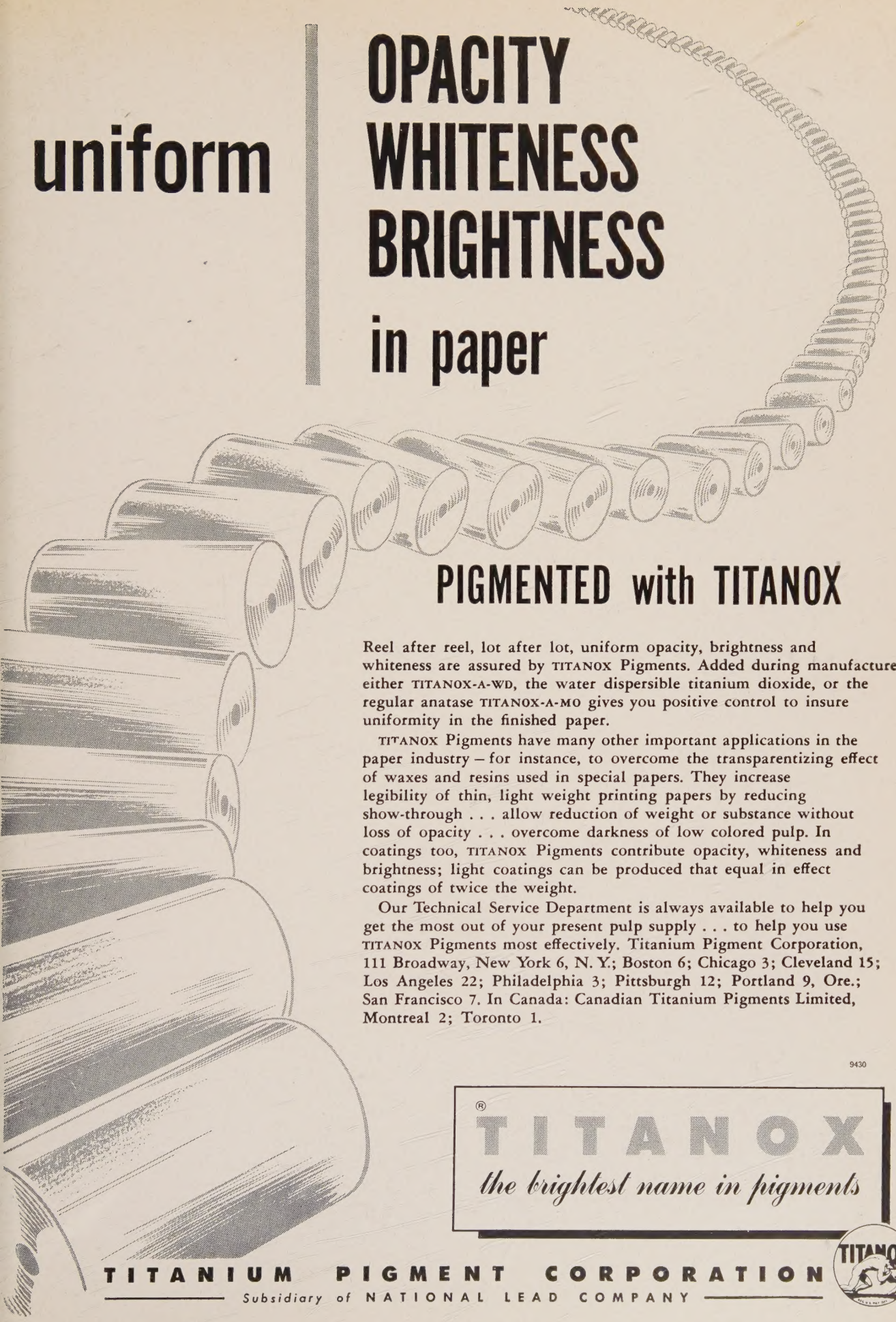

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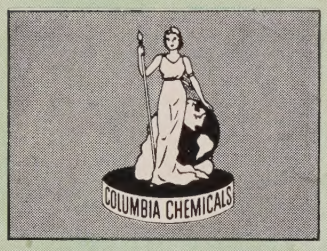

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## COLUMBIA-SOUTHERN CHEMICAL CORPORATION

SUBSIDIARY OF PITTSBURGH PLATE GLASS COMPANY

EXECUTIVE OFFICES:
Fifth at Bellefield, Pittsburgh 13, Pa.

**PLANTS:** Barberton, Ohio • Bartlett, California • Corpus Christi, Texas • Lake Charles, Louisiana • Natrium, West Virginia

**DISTRICT OFFICES:** Boston • Charlotte • Chicago • Cincinnati • Cleveland • Dallas • Houston • Minneapolis • New Orleans • New York Philadelphia • Pittsburgh • St. Louis